ASOCIACIÓN DE
QUÍMICOS DE GALICIA

Colexio Oficial de
Químicos de Galicia

SOCIEDADE
PORTUGUESA
DE QUÍMICA

XXVI ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA

CONGRESO INTERNACIONAL

2022

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FACULTAD DE QUÍMICA

XXVI ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA.
Noviembre 2022

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Manuel Rodríguez Méndez

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Facultade de Química da Universidade de Santiago de Compostela. Santiago de Compostela (España) 2022

El coordinador editorial declara que el contenido de los resúmenes científicos es de la entera responsabilidad de los respectivos autores.

PRÓLOGO

Foi no ano 1985, cando se estableceu un vínculo entre os químicos do norte de Portugal e de Galicia organizando aquel I ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA. Xa pasaron 37 anos daquel primeiro ENCONTRO que os profesores José Luis Costa Lima, José Luis Figueiredo, Gonzalo Vázquez Uña, Juan Vieites Bautista de Sousa, Pelayo Rubido Muñiz e José Varela Cardama puxeron en marcha.

Neste ano 2.022, e despois do parénteses que deixou a Covid-19, os ENCONTROS GALEGOS PORTUGUESES volven e acadan a súa vixésima sexta edición, coa mesma ilusión coa que aqueles pioneiros se puxeron en marcha e, tamén, coa mesma idea: Os ENCONTROS deben ser un punto de encontro entre os profesionais da química das dúas nacións irmáns.

Este ano celebrámolo na Facultade de Química da Universidade de Santiago de Compostela, que celebra o Centenario da súa fundación, e onde se celebrou o I ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA.

Sempre, sen perder de vista que a química é unha ciencia que abarca todas as facetas da vida e, tamén, sirve de base para outras disciplinas e, entre todas, poder facer unha sociedade mais xusta e próspera, este XXVI ENCONTRO INTERNACIONAL volve a unir a todas as persoas que fixeron e fan da química a súa profesión.

Non quero pechar este prólogo sen un emocionado recordo a todas as persoas que nos abandonaron por motivo da pandemia xerada pola Covid-19. Este Congreso dedicámolo a súa memoria. Permitídeme que teña un recordo especial para uns dos fundadores dos ENCONTROS, o Prof. José Luis Costa Lima que no ano 2021 deixounos definitivamente para, quen sabe, seguir outros camiños da química alí onde se encontre. O Prof. Costa Lima forma parte da historia dos ENCONTROS. Sempre estará con nos xa que o seu espírito de traballo, o seu saber e o seu carácter amable e conciliador fai del unha persoa que nunca esqueces. Grazas Profesor.

A Covid-19 puxo en valor a importancia da química or iso é importante que as persoas que estean a traballar nela, xa sexa na vertente científica como na súa aplicación empresarial ou docente, teñan un punto de encontro onde poñer en valor o seu coñecemento, onde establecer vínculos de colaboración futura para un maior avance da química e, en definitiva, da sociedade.

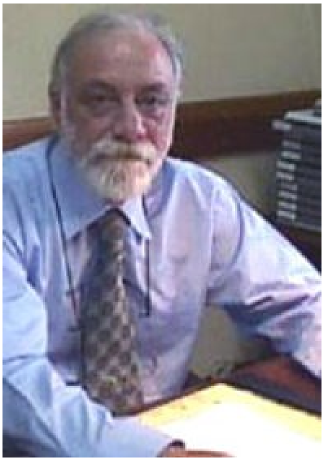
Espero que os desexos cos que vides a este XXVI ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA se vexan cumpridos. Grazas por vir e grazas aos pioneiros daquel ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA. Grazas Prof. Jose Luis Costa Lima.

Dr. Manuel Rodríguez Méndez
Decano Colexio Oficial de Químicos de Galicia.

In Memoriam
Prof. José Luís Costa Lima (1945-2022)

El Profesor José Luis Costa Lima fue uno de los pioneros y mentor de los ENCONTROS Luso-Galegos de Química que, desde 1984, se realizan alternativamente entre Galicia y el Norte de Portugal. Defensor de estos ENCONTROS ya que siempre reconoció el fuerte impacto que estos tienen en los jóvenes investigadores ya que, en muchos casos, es su debut como oradores científicos. Impulsarlos a estos jóvenes investigadores en estas tareas fue una de sus muchas formas de entrega y cariño hacia los jóvenes doctorandos. Esto se tradujo en los más de 60 doctorados que graduó a lo largo de estos años y a los que cariñosamente apodó como sus "hijos" científicos.

Fue miembro activo de la Sociedad Portuguesa de Química durante mucho tiempo. Sociedad en la que se volcó de una forma decidida y entusiasta, y en la que ocupó diferentes puestos. Así, fue Presidente de la División de Química Analítica (2002-2004), Vicepresidente de la Sociedad (2004-2006), Presidente de la Delegación de Oporto (2010-2015) y también Miembro de esta Delegación en diferentes ocasiones.



A lo largo de más de 50 años de actividad, siempre en la Facultad de Farmacia de la Universidad de Oporto (FFUP), fue autor y coautor de más de 500 artículos científicos y más de 3.000 comunicaciones a congresos y simposios nacionales e internacionales. También fue director de la misma Facultad de Farmacia durante los períodos 1998-2000 y 2010-2015. Se jubiló en 2015 y desde 2017 fue Profesor Emérito de la Universidad de Oporto.

El Prof. José Luís Costa Lima, tenía 76 años cuando falleció el 1 de febrero de este año 2022, para gran pena de todas las personas que le conocían y trataron a los que contagió su particular y cautivadora forma de ser, cuando ya se había comenzado la preparación de este XXVI Encuentro Galego-Portugués de Química.

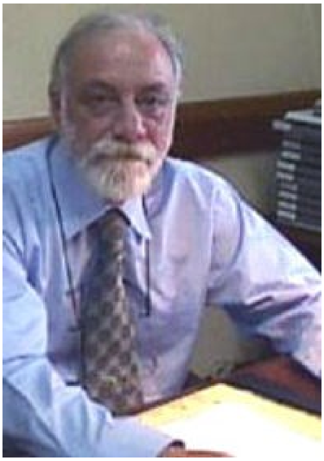
El Prof. José Luis Costa Lima siempre estará en la memoria de los que le conocimos y tratamos y forma parte de la historia de los ENCONTROS.

Descanse en paz.

Evocação
José Luís Costa Lima (1945-2022)

Foi um dos pioneiros e mentor dos Encontros Luso-Galegos de Química, que desde 1984, se realizam alternadamente entre a Galiza e o Norte de Portugal. Reconheceu neste encontro um forte impacto junto dos investigadores mais jovens, já que constituía em muitos casos a estreia deles como oradores científicos. Lançá-los nestas andanças foi uma das muitas formas de dedicação e afeto pelos jovens estudantes de doutoramento e que se traduziu naturalmente nos mais de 60 doutorados que formou ao longo dos anos e que carinhosamente apelidava dos seus "filhos" científicos.

Membro ativo da Sociedade Portuguesa de Química, desde longa data, contribuiu de forma empenhada a diferentes níveis tendo atuado como Vice-Presidente da Sociedade (2004-2006), Presidente da Divisão de Química Analítica (2002-2004), Presidente da Delegação do Porto (2010-2015) e também Vogal desta Delegação por diversas vezes.



Ao longo de mais de 50 anos de atividade, sempre na Faculdade de Farmácia da Universidade do Porto (FFUP), foi autor e coautor mais de 500 artigos científicos e mais de 3000 comunicações a congresso e simpósios nacionais e internacionais. Foi ainda diretor dessa mesma Faculdade de Farmácia por dois períodos (1998-2000 e 2010-2015. Jubilou-se em 2015 e desse 2017 que era Professor Emérito da Universidade do Porto.

O Prof. José Luís Costa Lima, contava 76 anos, quando faleceu a 1 de fevereiro deste ano de 2022, para grande pena de todos os que foram contagiados pela sua maneira de ser particular e cativante. Tendo iniciado connosco a preparação deste XVI Encontro Galego-Portugués de Química, será feita uma singela evocação da sua pessoa durante o mesmo.

Para sempre, terá um lugar na memória destes encontros e no nosso coração.

ÍNDICE

INTRODUCCIÓN

Un año más, y este año en especial, celebramos este congreso que reúne a los profesionales de la química no sólo de ambos lados del Miño, sino de todo el mudo. Este año se conmemora la 26ª Edición de este congreso internacional, en la misma ciudad donde nació y con la misma ilusión de la primera vez, aquel 14 de noviembre de 1985, cuando nos reunimos en Santiago de Compostela, en esta Facultad de Química que este año celebra el Centenario de su fundación. Este es un Congreso especial, es el primero que celebramos después de las restricciones originadas por la pandemia causada por la Covid-19. Con el mismo espíritu con el que se crearon estos ENCONTROS, y con el recuerdo puesto en aquellas personas queridas que ya no están con nosotros, nos volvemos a reunir para hablar de química.

Esta XXVI edición del ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA ha sido organizada bajo los auspicios del Colegio Oficial de Químicos de Galicia, Asociación de Químicos de Galicia y Sociedade Portuguesa de Química, sin olvidar a nuestros mentores y con un recuerdo especial para el Prof. José Luis Costa Lima que nos dejó para seguir nuevos rumbos, seguro que en la química.

COMISIÓN DIRECTIVA:

José Luis Francisco Fuentes. Colegio Oficial de Químicos de Galicia. España
Prof. Joaquim Luis Faria. Sociedade Portuguesa de Química, Faculdade de Engenharia, Univ. Porto, Portugal
José Ramón Bahamonde Hernando. Colegio Oficial de Químicos de Galicia. España.
Prof. Baltasar Romão de Castro. Sociedade Portuguesa de Química, Faculdade de Ciencias, Univ. Porto, Portugal
Manuel Rodríguez Méndez. Colegio Oficial de Químicos de Galicia.
Prof. Dr. Carlos M.M. Afonso. Sociedade Portuguesa de Química, Faculdade de Farmácia, Univ. Porto, Portugal
Prof. Dr. Victor A. Pereira Freitas. Sociedade Portuguesa de Química, Faculdade de Ciências, Univ. Porto, Portugal

COMISIÓN CIENTÍFICA:

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Prof. María de Los Ángeles Peña Gallego. Dpto. Química Física, Univ. de Vigo
Prof. Dr. José María Fernández Solís. Escuela Politécnica Enxeñaría de Ferrol, Univ. da Coruña
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Prof. Dr. Victor A. Pereira Freitas. Sociedade Portuguesa de Química, Faculdade de Ciências, Univ. Porto, Portugal

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Juan José Sanmartín Rodríguez. Colegio Oficial de Químicos de Galicia
Juan José Losada López (ENCE)
Francisco Javier Becerra García. Colegio Oficial de Químicos de Galicia

Manuel Rodríguez Méndez. Colegio Oficial de Químicos de Galicia y la Comisión Organizadora del XXVI Encontro Internacional Galego-Portugués de Química, desea manifestar su agradecimiento a las siguientes instituciones:

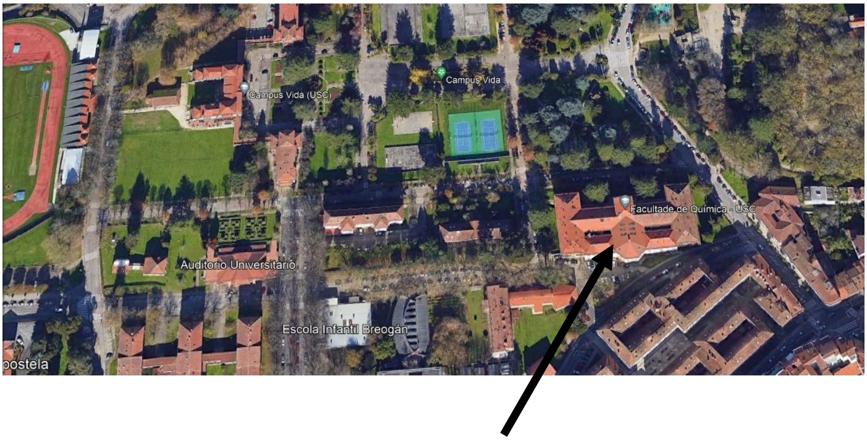
LOCALIZACIÓN DEL XXVI ENCONTRO INTERNACIONAL GALEGO PORTUGUÉS DE QUÍMICA

Santiago de Compostela é a capital da Comunidade Autónoma de Galicia. A súa zona antiga é Patrimonio da Humanidade dende o ano 1.985. Xunto con Xerusalem e Roma, Santiago é un centro de peregrinación do cristianismo. Dende a etapa medieval, chegase a Santiago dende diversas rutas de peregrinación, dende o centro de Europa a mais longa, ata a súa Catedral adeicada ao Apostolo Santiago. Centos de miles de peregrinos de todo o mundo veñen peregrinando ata a súa Catedral.

Santiago de Compostela ten unha población de case 96.456 habitantes (INE 2017), que pode duplicarse durante o curso universitario.

INFORMACIONES VARIAS

El Encontro se celebrará en el edificio de la Facultad de Química de la Universidad de Santiago de Compostela, situado en la Avenida das Ciencias s/n, en el Campus Universitario, 15701 Santiago de Compostela.



Facultad de Química

LA FACULTAD DE QUÍMICA

La Facultad de Química de la Universidad de Santiago de Compostela está ubicado en el Campus de la Universidad. Está en un edificio construido en la segunda mitad del siglo XX. Este año 2.022, la Facultad celebra el Centenario de su creación.

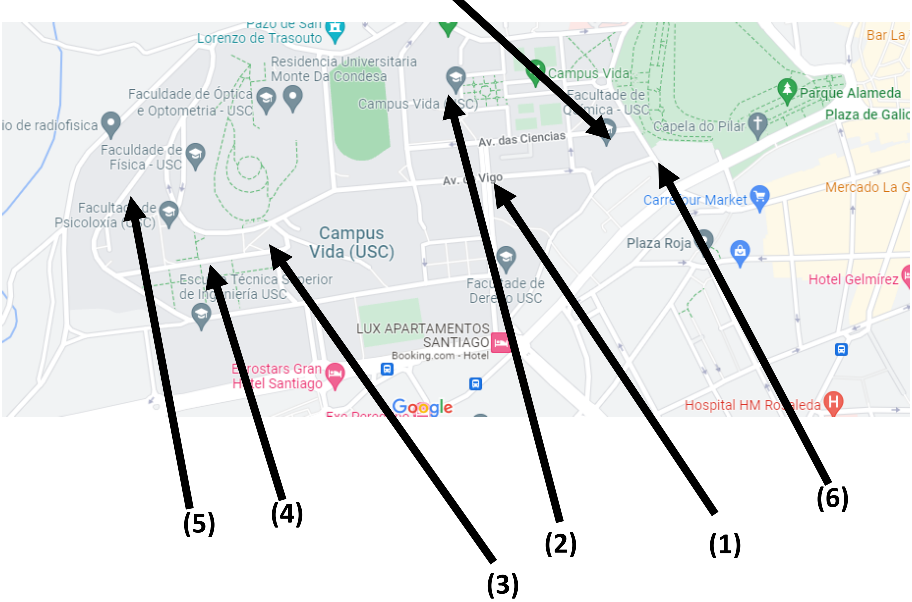
https://www.usc.gal/gl/centro/facultade-quimica

PARA COMER LOS DÍAS DEL CONGRESO:

La Facultad de Química está ubicado en el Campus de la Universidad, lugar donde se puede comer a un precio muy asequible para todas las personas asistentes al Congreso. Los lugares más próximos al Congreso son:

- **(1)** Comedor Universitario.
- **(2)** Colegio Mayor Fonseca.
- **(3)** Facultad de Matemáticas.
- **(4)** Escuela Técnica Superior de Ingeniería
- **(5)** Comedor Facultad Ciencias de la Educación.
- **(6)** Zona restauración fuera del Campus

FACULTAD DE QUÍMICA



INFORMACIÓN SOBRE EL CONGRESO

RECEPCIÓN

La oficina de información y la recepción para retirar la documentación del Encontro, estará localizada en el vestíbulo de la Facultad de Química, en la planta baja. Permanecerá abierta durante todos los días de su celebración.

EQUIPAMIENTO DE PROYECCIONES

Las salas de conferencias están equipadas con ordenador y cañón de proyección. Cada orador deberá transferir el fichero de su presentación al ordenador de la sala que le corresponda, con la antelación suficiente. Siendo aconsejable se realice en la sesión anterior.

PRESENTACIONES ORALES

Las conferencias plenarias tendrán una duración de 45-50 minutos más 10 minutos para preguntas.

La duración de las comunicaciones orales será de 10 minutos más 5 minutos para resolución de dudas. Se solicita a todos los oradores que cumplan el tiempo estipulado, a fin de evitar retrasos en el programa.

Se recomienda que las presentaciones se hagan en formato pdf.

POSTERS

Deberán colocarse el primer día, primera sesión y retirarse el último, tras el acto de clausura, por los propios autores de la comunicación. Se solicita a los autores de los trabajos presentados, estén presentes junto a los mismos durante la sesión de discusión.

SALAS DEL CONGRESO

El congreso tendrá lugar en 4 salas de la Facultad de Química de la Universidad de Santiago de Compostela. Tres salas están situadas en la planta baja y, la cuarta sala, en la segunda planta. Los posters se colocarán en los pasillos de la segunda planta y en la planta baja.

Planta Baja

- El Aula Magna (A) es la sala donde se realizará la inauguración y clausura del Congreso y, también donde se presenten las Ponencias Plenarias del Congreso. También se usará para ponencias del Congreso.
- Sala B. Es el Aula de Química Técnica. Se utilizará para ponencias del Congreso.
- Sala C. Es el Aula de Química-Física. Se utilizará para ponencias del Congreso.

Segunda Planta

- Sala D. Es el Aula de Química General. Se utilizará para ponencias del Congreso.

CENA DEL ENCONTRO

La cena del ENCONTRO se celebrará el día 17 de noviembre a las 21:30 horas en el Comedor de la Hospedería del Seminario Mayor (http://sanmartinpinario.es/). El coste de la cena es 25,00 euros.

La Hospedería San Martín Pinario está situada en el centro histórico de Santiago de Compostela, en la Plaza de la Inmaculada nº 3, frente a la Catedral. Es un edificio empezado a construir a finales del Siglo XVI. Es un edificio histórico y, después del Monasterio del Escorial, es el mayor de España. Cerca del edificio hay una zona de cafeterías muy típicas de Santiago de Compostela.

PROGRAMA DEL XXVI ENCONTRO INTERNACIONAL GALEGO PORTUGUÉS DE QUÍMICA

SALAS		Planta
A	Aula Magna	P. Baja
B	Química Física	
C	Química Técnica	
D	Química General	2ª

DÍA	HORA	SALAS				
		PLENARIAS SALA A	A	B	C	D
16	10:00 - 12:00	INSCRIPIÓN Y RECEPCIÓN				
	12:00- 12:30	SESIÓN DE APERTURA. Aula Magna				
	12:30-13:30	CONFERENCIA PLENARIA de APERTURA. Aula Magna				
	13:30-15:00	COMIDA				
	15:00		QS01	AMB01	ALM01	CAT01
	15:15		QS02	AMB02	ALM02	CAT02
	15:30		QS03	AMB03	ALM03	CAT03
	15:45		QS04	AMB04	ALM04	CAT04
	PAUSA: 5 minutos					
	16:05		QS05	AMB05	ALM05	CAT05
	16:20		QS06	AMB06	ALM06	CAT06
	16:35		QS07	AMB07	ALM07	CAT07
	16:50		QS08	AMB08	ALM08	CAT08
	17:05-18:00	COFFEE BREAK + POSTERS				
	18:00-19:00	CP1				
	19:00		QS09	AMB09	ALM09	CAT09
	19:15		QS10	AMB10	ALM10	CAT10
	19:30		QS11	AMB11	ALM11	CAT11
	19:45		QS12	AMB12	ALM12	CAT12
	20:00		QS13	AMB13	ALM13	CAT13
	20:15		QS14	AMB14	ALM14	CAT14

DÍA	HORA	SALAS				
		PLENARIAS SALA A	A	B	C	D
17	9:00		QS15	AMB15	ALM15	CAT15
	9:15		QS16	AMB16	ALM16	CAT16
	9:30		QS17	AMB17	ALM17	CAT17
	9:45		QS18	AMB18	ALM18	CAT18
	10:00		QS19	AMB19	ALM19	CAT19
	10:15		QS20	AMB20	ALM20	CAT20
		PAUSA: 5 minutos				
	10:35		QS21	AMB21	ALM21	CAT21
	10:50		QS22	AMB22	ALM22	CAT22
	11:05		QS23	AMB23	ALM23	QO01
	11:20		QS24	AMB24	ALM24	QO02
	11:35		QS25	AMB25	ALM25	QO03
	11:50		QS26	AMB26	ALM26	QO04
	12:05-12:45	COFFEE BREAK + POSTERS				
	12:45-13:30	CP2	🟦			
	13:30-15:00	COMIDA				
	15:00		QS27	AMB27	ALM27	QO05
	15:15		QS28	AMB28	ALM28	QO06
	15:30		QS29	AMB29	ALM29	QO07
	15:45		QS30	AMB30	ALM30	QO08
	16:00		QS31	AMB31	ALM31	QO09
	PAUSA: 5 minutos					
	16:05		QS32	AMB32	ALM32	QO10
	16:20		QS33	AMB33	NN01	QO11
	16:35		QS34	AMB34	NN02	QO12
	16:50		QS35	AMB35	NN03	QO13
	17:10		QS36	QA01	NN04	QO14
	PAUSA: 5 minutos					
	17:20-18:00	COFFEE BREAK + POSTERS				
	18:00-18:45	CP3	🟦			
	18:45	HOMENAJE COSTA LIMA				
	19:15		**QA25**	QA02	NN05	QO15
	19:30		**NN19**	QA04	NN06	QO16
	19:45		**QA19**	QA05	NN07	QO17
	20:00		**NN20**	QA06	NN08	QO18
	20:15		**QA26**	QA07	🟥	🟥
	21:45	CENA DEL ENCONTRO				

DÍA	HORA	SALAS				
		PLENARIAS SALA A	A	B	C	D
18	9:00		QS37	QA08	NN09	QO19
	9:15		QS38	QA09	NN10	QO20
	9:30		QS39	QA10	NN11	QO21
	9:45		QS40	QA03	NN12	QO22
	10:00		QS41	QA11	NN13	QO23
	10:15		QS42	QA12	NN14	QO24
	PAUSA: 5 minutos					
	10:35		QS43	QA13	NN15	BB01
	10:50		QS44	QA14	NN16	BB02
	11:05		QS45	QA15	NN17	BB03
	11:20		QS46	QA16	NN18	BB04
	11:35		QS47	QA17	POL01	BB05
	11:50		QS48	QA18	POL02	IND01
	12:05-12:45	COFFEE BREAK + POSTERS				
	12:45-13:30	CP4				
	13:30-15:00	COMIDA-ALMUERZO				
	15:00		QS49	QA20	QF01	IND02
	15:15		EDU01	QA21	QF02	IND03
	15:30		EDU02	QA22	QF03	IND04
	15:45		EDU03	QA23	QF04	IND05
	16:00		QI01	QA24	QF05	IND06
	16:15		QI02	QT01	QF06	IND07
		PAUSA: 5 minutos				
	16:35		QI03	QT02	QF07	IND08
	16:50		QI04	QT03	QF08	IND09
	17:05		QI05	QT04	QF09	IND10
	17:20		QI06	QT05	QF10	IND11
	17:35		QI07	QT06	QF11	IND12
	17:50		QI08	QT07	QF12	IND13
	PAUSA: 5 minutos					
	18:10	CLAUSURA				

RELACIÓN DE CONFERENCIAS PLENARIAS

CONFERENCIA APERTURA:

Prof. Doctor M. Stanley Whittingham
Premio Nobel de Química año 2.019
Chemistry Department, Binghamton University

The Critical Role of Energy Storage in the Electric Economy and Overcoming Climate Change

CP 1 **Prof. Doctora Maria da Conceiçao Rangel**
REQUIMTE-LAQV, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto. PORTUGAL

Hydroxypyridinones: Chelators to Life Sciences

CP 2 **Prof. Doctora María Dolores Pérez Meiras**
Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, Santiago de Compostela, Spain

Aryne Chemistry in the Graphene Era

CP 3 **Prof. Doctor José M. Andrade-Garda**
Grupo de Química Analítica Aplicada. Departamento de Química. Campus da Zapateira. Universidade da Coruña, A Coruña, 15071, A Coruña, Spain

Determination of microplastics in environmental samples

CP 4 **Prof. Doctor José Luis Capelo Martinez**
Department of Chemistry. Faculty of Science and Technology. NOVA University of Lisbon. PORTUGAL
Prescriptomics

RELACIÓN DE COMUNICACIONES

CONFERENCIAS PLENARIAS

CONFERENCIA DE APERTURA

Profesor Doctor M. Stanley Whittingham

The Critical Role of Energy Storage in the Electric Economy and Overcoming Climate Change

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CP 3 **Prof. Doctor José M. Andrade-Garda**

Determination of microplastics in environmental samples

CP 4 **Prof. Doctor José Luis Capelo Martinez**

Prescriptomics

COMUNICACIONES

QUÍMICA ALIMENTARIA

Oral

ALM01	Desenvolvimento de um novo vinagre espirituoso de origem vínica.
ALM02	Mycotoxins and inorganic arsenic in rice: the Portuguese scenario and human risk assessment in the worldwide context.
ALM03	Inhibición de la actividad microbiana y la alteración lipídica en productos marinos mediante empleo de extractos de la macroalga *Bifurcaria bifurcata.*
ALM04	Diferenciación quimiométrica de tequilas blancos en función de sus espectros infrarrojos.

ALM05 Plantas condimentares do género *Thymus* como uma alternativa natural para conservação de alimentos.

ALM06 Caracterização dos resíduos de *Brassica oleracea* L. para obtenção de um potencial ingrediente natural.

ALM07 Caracterización detallada de la harina del mesocarpio de *Attalea speciosa* y su aplicación para el desarrollo de nuevos productos de panadería.

ALM08 Risk assessment of nine coccidiostats in commercial and home raised poultry.

ALM09 Efeito de bioestimulantes vegetais nos perfis nutricionais e químicos de *Corylus avellana* L. (avelã).

ALM10 Efeito de bioestimulantes vegetais nos perfis nutricionais e químicos de amêndoa [*Prunus dulcis* (Miller) D. A. Webb].

ALM11 Composição química e bioatividades do epicarpo de *Nephelium lappaceum* L.

ALM12 Dietary polyglycosylated anthocyanins, the smart option? Towards their stability and bioavailability.

ALM13 Comparação do efeito de diferentes poliaspartatos de potássio na estabilização tartárica e na filtrabilidade do vino.

ALM14 Multielement analysis as a discriminating tool of PDO and PGI food products.

ALM15 *Adansonia digitata* L. (mukua): um possível alimento funcional.

ALM16 H*aematococcus pluvialis* como aditivo en la coloración y mejora de las propiedades organolépticas y nutricionales de alimentos.

ALM17 Flavylium-based host-guest systems for biogenic amine sensing during food spoilage.

ALM18 Effects of gastrointestinal digestion on the bioactive properties and phlorotannin profile from *Laminaria digitata.*

ALM19 Application of data mining techniques to unveil contaminants occurrence in food.

ALM20 Caracterização química e propriedades bioativas de resíduos industriais da produção de óleo de noz (*Juglans regia* L.).

ALM21 Avaliação de subprodutos de soja (*Glycine max*), uma potencial fonte de nutrientes e compostos bioativos.

ALM22 *Sandoricum koetjape* fruit juice inhibits 5-lipoxygenase and interferes with the inflammatory response of activated BV-2 cells.

ALM23 Combinação de diferentes regimes de fertilização e irrigação para a produção de cardo dourado (*Scolymus hispanicus* L.) de alto valor nutricional e mineral.

ALM24 Quantificação e caracterização do conteúdo de polifenóis em produtos de maçã.

ALM25 Propiedades nutricionales y bioactivas de la frambuesa roja Kweli® cultivada en Portugal.

ALM26 Optimización de la extracción asistida por microondas de aceite de subproductos de pescado y evaluación de su calidad nutricional.

ALM27 Delivery vehicles for resveratrol incorporation in bread.

ALM28 Obtenção otimizada de extratos bioativos de casca de marmelo: Uma fonte alternativa de conservantes naturais.
ALM29 Bioprospecting sequential extraction to obtain valuable compounds from brown macroalgae *Fucus vesiculosus.*
ALM30 Nutritional, chemical and bioactive characterization of *Peumus boldus* L.
ALM31 Antimicrobial activity of rosemary, eucalyptus and propolis individual and mixed extracts.
ALM32 Chemical content and antioxidant activity variation during cherry development stages after application of biostimulants.

Póster/Panel

ALM33 Obtención de lípidos polares a partir de desechos industriales de pulpo (*Octopusvulgaris*) mediante empleo de disolventes de tipo GRAS.
ALM34 Use of protective starter cultures and plant essential oils to reduce preservatives in traditional Portuguese sausages: “*Chouriço*” and “*Alheira*”.
ALM35 Evaluation of the physico-chemical, microbiological and sensory characteristics of sheep's and goat's ice cream, produced with UF concentrated second cheese whey.
ALM36 Comparison of the amino acid profile of two by-products of the coffee industry: pulp and husk.
ALM37 Enfoques integrados para el impulso socioeconómico de la producción y consumo sostenible de hongos de Montesinho.
ALM38 Antioxidant capacity of *Palaemon serratus* and *Palaemon varians* shell waste.
ALM39 Perfil fenólico e avaliação da atividade antioxidante e antimicrobiana do epicarpo de *Sicana odorifera* (Vell.*)* Naudin.
ALM40 Extraction of bioactive compounds from three varieties of date by-products through sustainable methodologies.
ALM41 Valorização de biorresíduos da produção de sumo de laranja: extração de ácido cítrico.
ALM42 Collagen determination in fish skin: development of a flow analysis system for quantification of hydroxyproline.
ALM43 Phlorotannins-rich extract from *Laminaria digitata* for the development of a functional granola towards prevention of Diabetes mellitus.
ALM44 Multiple mycotoxin analysis method for rice.
ALM45 Promising bioactive properties from *Moringa oleifera* seed cake protein hydrolysates.
ALM46 Evaluation of phenolic compounds present in prunings of native Galician olive trees.
ALM47 Bioaccessibility of phenolic compounds from Galician olive leaf infusions.

ALM48	Caracterização química de uma massa alimentícia com bagaço de azeitona.
ALM49	Pasta de bagaço de azeitona: ingrediente promissor para a indústria cosmética e alimentar?.
ALM50	Reliable in-line determination of the protein, fat, sodium and salt content in pasty doughs through near infrared spectroscopy and chemometrics.
ALM51	In-line aplication of near infrared spectroscopy for the classification of doughs in bakery.
ALM52	Amino acid profile: comparison among coffee silverskin and green and roasted beans.
ALM53	Comparison of the amino acid profile of two by-products of the coffee industry: pulp and husk.
ALM54	Maltodextrin Microencapsulation of Phenolic-rich Fractions of *Gunnera tinctoria* Extracts.
ALM55	Occurrence of Coccidiostats in Portuguese Eggs.
ALM56	Antitumoral Activity of *Gunnera tinctoria* Extracts on a Pancreatic cell line.
ALM57	Effect of pre-harvest foliar application of seaweed and glycine-betaine-based biostimulants on blueberry quality.
ALM58	Determination of CO_2 in roasted coffee using a TAS optimized with super-modified simplex.
ALM59	Phenolic compounds and antioxidant and cytotoxic properties of maritime pine (*Pinus pinaster* Ait.) bark extracts.
ALM60	Effects of different treatments on the phenolic composition of acorn extracts from *Quercus robur* and *Quercus rotundifolia.*
ALM61	Synergy and antagonism: a different interpretation of the interactions between the antioxidants used as food additives.
ALM62	*Sargassum m*uticum - Screening of its bioactive potential.
ALM63	Fermentation of olive pomace paste to obtain an innovative antioxidant food ingredient.
ALM64	Study of the antioxidant, antimicrobial and anti-inflammatory activities of two *Euphorbia* species.
ALM65	*Verbascum sinuatum* L.: Potential source of natural antioxidant compounds for food and pharmaceutical industries.
ALM66	Exploring the potential of *Citrus aurantium* L. flowers as a source of antioxidant compounds.
ALM67	Biological properties of *Hypericum sampsonii* and *Hypericum japonica*: comparison of the antioxidant, anti-inflammatory and antimicrobial activity.
ALM68	Insights of honey DNA extraction methods for plant species identification of honey from Natural Park of Montesinho.

ALM69 Efeito do método de extração no perfil fenólico e na atividade antioxidante de extratos de casca de marmelo.

ALM70 Priming with *Laminaria* extract to boost tomato performance and mitigate drought effects.

ALM71 Algae blend on lambs diet: Effects on rumen and colon fermentation pattern.

ALM72 Antioxidant activity of sweet cherry fruits (cv. *Lapins*) after foliar application of a seaweed extract.

ALM73 Effects of the sowing date on the production of alkaloids in the seeds of three *Lupinus* species.

ALM74 Identificação e otimização da extração de compostos fenólicos de cascas de abóbora ‘Butternut squash’.

ALM75 Simultaneous determination of bisphenols, personal care products, and pesticide residues in fish species from Portuguese estuaries.

ALM76 Nutritional value of European seabass (*Dicentrarchus labrax*) muscle is affected by algae blend supplementation.

ALM77 On-farm dietary *Chlorella vulgaris* supplementation affects *Longissimus lumborum* fatty acid profile of finishing pigs.

ALM78 Recuperação de subprodutos da indústria alimentar para extração otimizada de compostos fenólicos.

QUÍMICA AMBIENTAL Y SOSTENIBLE

Oral

AMB01 Remoção de parabenos por processos Fenton e foto-Fenton.

AMB02 Chemical contamination in “O Burgo” estuary (Galicia). Lithogenic and anthropogenic inputs to the sedimentary reservoir.

AMB03 Combination of coagulation-flocculation-decantation with Fenton-based processes for agro-industrial wastewater treatment.

AMB04 Treatment of a winery wastewater by a peroxymonosulfate/cobalt/ UV system.

AMB05 Determinación de normalizadores para elementos traza en el sedimento del continuum afluente-río-estuario-ría (Ulla-Arousa, Galicia).

AMB06 Vine-canes-based extracts as antioxidants for biodiesel production: A Life Cycle Assessment study.

AMB07 Removal of perfluoroalkylated substances (PFAS) with a broad spectrum of alkyl chain lengths (C1-C13) using a boron-doped diamond electrode and real aqueous matrices.

AMB08 A Sustainable Methodology for the Preparation of HIV Protease Inhibitors to Tackle Viral Resistance.

AMB09	Controlled thermal degradation of Polyoxometalate@Zeolitic Imidazolate Framework composites towards novel oxidation catalysts.
AMB10	Biomass-based materials for estrogens adsorption from water: production methods and their characterization.
AMB11	Green Chemistry in the Pharmaceutical Industry.
AMB12	Predicting DDT past and future contamination from a local source with a new gridded dynamic multimedia fate model.
AMB13	Evaluation of activated carbon obtained from olive stones for the removal of sertraline from waters.
AMB14	Remediación y recuperación de fósforo con materiales nanoestructurados con potencial reaprovechamiento como fertilizantes.
AMB15	Geoquímica e biodisponibilidade do Cu em solos de manguezais da Baía de Todos os Santos, Bahia, Brasil.
AMB16	Valorización de sub-productos de la industria agroalimentaria gallega a través de la Química Verde.
AMB17	Development of a Sustainable Recovery Process of Indium from Liquid Crystal Displays of Smartphones Waste.
AMB18	Iron determination in natural waters using a synthesized 3-hydroxy-4-pyridione ligand in a newly developed µfluidic paper-based device.
AMB19	Pre-treatment to increase gold recovery from integrated circuits of smartphones wastes.
AMB20	Valorization of vine shoots to extract lignin – chemical and structural characterization.
AMB21	Bioacumulação de Cu em tecidos de *Ucides cordatus* em manguezais da Baía de Todos os Santos, Bahia, Brasil.
AMB22	Geopolímeros desde residuos de tierras diatomeas para el tratamiento de aguas residuales de la industria vitivinícola.
AMB23	Potential of macroalgae to remove rare earth elements from contaminated Waters.
AMB24	Glyphosate and Aminomethylphosphonic acid adsorption in soils.
AMB25	Searching for a new generation of environmentally compatible antifouling agents.
AMB26	Screening of the main factors affecting the microwave-assisted extraction (MAE) of phenolic compounds from cork industry waste.
AMB27	Comparison of Advanced Tertiary Treatments for Pharmaceuticals Removal from a Municipal Wastewater.
AMB28	Low-cost natural biosorbents for the treatment of contaminated waters.
AMB29	Silver nanoparticles bioaccumulation assay in marine organisms.

AMB30 Removal of anthropogenic pollution markers with a nitrogen-doped reduced graphene oxide-PVDF membrane.

AMB31 Ohmic heating-assisted regioselective sulfonation of aniline: synthesis of sulfanilic acid.

AMB32 New Trends in Bio-Based Aerogels for CO_2 conversion.

AMB33 Extractabilidade de metais pesados en solos urbanos de Santiago de Compostela.

AMB34 Lipidic profile of *Salicornia perennis* in different salt marshes of the Ria de Aveiro.

AMB35 Optimizing the characterization of microplastics when ir spectrometry using a quantum cascade laser is used.

<u>Póster/Panel</u>

AMB36 Prospecção fitoquímica das folhas de *Dizygostemon riparius* (Plantaginaceae) morfotipo floral branco.

AMB37 Evaluación de la degradación del benzo(a)pireno por microalgas y sus extractos enzimáticos por medio de metodología SPE-HPLC.

AMB38 Ecotoxicity evaluation of treated wastewaters using *Daphnia magna* and *Raphidocelis subcapitata.*

AMB39 Microplastics in Portuguese agricultural soil: identification by Raman Spectroscopy.

AMB40 Carbon Materials as Renewable Catalysts for CO_2 Addition to Epoxides.

AMB41 Plantas aquáticas como bioindicadores da poluição de sistemas estuarinos por metais pesados.

AMB42 Degradación de láminas conductoras transparentes de óxido de indio dopado con estaño (ITO).

AMB43 Characterization TiO_2 chemically deposited on ITO substrate for solar cells.

AMB44 Supervised classification combined with genetic algorithm variable selection for microplastics measured by infrared spectrometry.

AMB46 Study of carbon matrix supported on carbon fiber as gas diffusion electrode for electrogeneration of oxidants species using a flow-by reactor.

AMB47 La importancia de la gestión del excedente textil en el nuevo marco de la Ley de Residuos.

AMB48 Zn-Doped Carbon Catalysts Highly Efficient for Benzodiazepine Synthesis: Tires Valorization.

AMB49 Quinolines synthesis promoted by carbon catalysts from polyethylene terephthalate (PET). Wastes valorisation.

AMB50 (Photo)catalytic transformation of HMF into value-added products.

AMB51 (Photo)catalytic reduction of 4-NPh using TiO_2 from Cork Powder Fly Ashes.

AMB52 High removal of paracetamol by catalytic wet peroxide oxidation with carbon-coated magnetic nanoparticles.

AMB53 A microwave-assisted approach for cellulose extraction from Eucalyptus and Pine tree waste products.

AMB54 Temporal trends of Polycyclic Aromatic Hydrocarbons in soils impacted by a prescribed fire.

AMB55 Impact of a synthetic aminated 3,4-dioxygenated antifouling xanthone in human retinal cells.

AMB56 Mejora de la capacidad de adsorción de *hydrochar* de alperujo en la eliminación de compuestos farmacéuticos mediante la funcionalización en un solo paso con grupos amino.

AMB57 Efecto del envejecimiento marino natural *vs* simulado en el contenido metálico de microplásticos de biopolímeros.

AMB58 Cork by-products extracts with added-value for the cosmetic industry.

AMB59 Hexachlorocyclohexane adsorption assays on two moss species for biomonitoring purpose.

AMB60 Application of Advanced Oxidation Processes to Industrial and Agro-industrial Wastewater for Energy Production: a Review.

AMB61 A novel, green and fast chromatographic method to quantify nystatin in pharmaceutical samples: development and validation.

AMB62 Excess sludge treatment by dewatering and consecutive adsorbent production.

AMB63 Novel Pitavastatin Calcium Forms: Insights Into a Complex Solid State System.

AMB64 Bromothymol Blue and Bromocresol Green removal using chitin as a sorbent material: pH, kinetic and equilibrium studies.

AMB65 Development of Potential Antibacterial Agents through Sustainable Synthetic Strategies.

AMB66 Highly efficient transition metal-doped carbon catalysts for the selective synthesis of quinoxalines.

AMB67 Silica-supported molybdenum oxide catalysts for efficient and selective synthesis of quinoxalines.

AMB68 Adsorption of volatile fatty acids with activated carbons produced from olive pomace.

AMB69 Production and Characterization of Geopolymeric Mortars From Diatomaceous Earth.

AMB70 A computer vision approach in identifying foam consolidation.

AMB71 New functionalized alginate aerogel materials as potential removal agents of diclofenac in water.

AMB72 Inventory of Best Available Techniques candidates for Bioenergy with Carbon Capture, Storage and Utilization.

AMB73 Distribución de metais traza en perfís de solos urbanos de Santiago de Compostela.

AMB74 Influence of mercury from wildfires on mussels: a preliminary study in the Galician estuaries

AMB75 Vanadium Redox Flow batteries and their effect on grid stability.

AMB76 Determination of bioactive compounds from cork powder extracts by high-performance liquid chromatography.

AMB77 Sustainable Use of Batteries According to the Electricity Prices: Energy Management and Lifespan

BIOQUÍMICA Y BIOTECNOLOGÍA

Oral

BB01 Flavonoids as potential anti-obesity compounds: Inhibition of pancreatic lipase.

BB02 Building enzymatic nanoreactors using the IC-Tagging system: a powerful methodology for the stabilization and immobilization of enzymes with industrial interest.

BB03 Soft Free-Standing Membranes made of Chitosan and Alginate as Sustainable Nano-Reservoirs for Controlled Drug/Therapeutics Delivery.

BB04 Development of an enzyme replacement therapy based on a stabilized version of *Av*PAL using the IC-Tagging system.

BB05 Downstream processing of L-asparaginase through silica-based supported ionic liquid-like phase materials

Póster/Panel

BB06 Development of an enzymatic biosensor based on boron-doped diamond Surface.

BB07 The effect of calcium in the fermentation of white cabbage and Salicornia.

BB08 Development of a novel phagomagnetic separation protocol coupled with isothermal DNA amplification for a rapid *Campylobacter* detection.

BB09 Innovative phagomagnetic-assisted isothermal DNA amplification system for endpoint electrochemical detection of *Listeria monocytogenes.*

BB10 Identificación de novos inhibidores do receptor de coláxeno GPVI mediante un ensaio fenotípico.

CATÁLISIS

Oral

CAT01 Ionic Liquid-based POM@ZIF-8 as a catalyst for simultaneous desulfurization and denitrogenation processes.

CAT02 Catalytic membranes based in polyoxometalates for fuel desulfurization.

CAT03 Metal Organic Frameworks as adsorbents with catalytic properties promoting Advanced Oxidation Regeneration.

CAT04 Shrimp shells derived electrocatalysts towards oxygen reduction reaction.

CAT05 Self-assembled binary structures of Fe(III) and metal-free porphyrins for sunlight-assisted catalytic hydrogenation.

CAT06 Binary Mn(III) and Fe(III) porphyrin nanostructured materials in catalytic hydrogenations assisted by sunlight.

CAT07 Fabrication of a new Fe_3O_4@TiO_2 composite as a magnetic recoverable photocatalyst for degradation of water pollutants.

CAT08 Hydroformylation-based reactions using chiral binaphthyl monophosphite ligands.

CAT09 Graphitic carbon nitride coated onto alumina foams as an efficient supported visible-active photocatalyst for the degradation of pharmaceutical substances in water.

CAT10 *Hydrochars* dopados con nitrógeno para la activación del peroximonosulfato: evaluación para el tratamiento de aguas residuales.

CAT11 Tri-hybrid catalyst combining polyoxometalates, MOF and silica for the desulfurization of heavy fuel oil.

CAT12 Electrocatalytic performance of biochar-based catalysts.

CAT13 Promoted Ni/BEA catalysts for dry reforming of methane.

CAT14 Sustainable strategies for electrochemical CO_2 reduction.

CAT15 Remarkable photocatalytic production of H_2O_2 using metal-free doped carbon nitride.

CAT16 Highly efficient antimicrobial and self-cleaning cotton fabrics coated with graphitic carbon nitride.

CAT17 Parabens removal using UiO-66-NH_2 under solar light

CAT18 C_3N_4-SiO_2 nanocomposites as visible light-active photocatalytic treatments for building materials.

CAT19 Ir(I)-catalyzed enantioselective hydrocarbonation of allenes: access to fused heterocycles bearing quaternary stereocenters.

CAT20 Modulating the performance of electrocatalyst materials.

CAT21 Sustainable synthetic catalytic processes for transformation of eugenol into potential fragrances.

CAT22 Asymmetric Michael addition of nitromethane to chalcones mediated by chiral organocatalysts in ionic liquids.

Póster/Panel

CAT23 Synthesis of Cu_2ZnSnS_4 by hydrothermal method and its application as Congo Red photocatalyst.
CAT24 Síntese de nanopartículas de óxido de ferro III dopadas e não dopadas com rutenio utilizando extrato hidro-alcoólico da folha de *Syzygium cumini* (L.) Skeels (jamelão).
CAT25 Synthesis of nanostructured organometallo-titania hybrid materials and their application in dye degradation.
CAT26 Iron-based metal organic framework as an active electrocatalyst for water splitting reactions.
CAT27 Sugar cane-derived solid acid catalysts for the production of fuel additives via glycerol esterification.
CAT28 Green diesel production *via* hydrogen free sustainable catalytic processes.
CAT29 Development of oxidative catalytic processes in continuous flow chemistry for drug degradation.
CAT30 Photocatalytic transformation of biomass-derived compounds into valuable products.
CAT31 Degradación enzimática del antibiótico sulfametoxazol mediante lacasa *Trametes Versicolor* empleando siringaldehído como mediador redox.
CAT32 Carbocatalizadores híbridos GO-TiO_2 y G-GP-TiO_2 para reducción del potencial de formación de subproductos de desinfección mediante PAO basados en ozono.
CAT33 Shrimp shells waste as bioresource for antioxidant extracts and N-doped carbon materials.
CAT34 Feasibility of continuous flow photo-Fenton treatment using a magnetically separable Fe_3O_4/TiO_2 catalyst.
CAT35 Comparative study on the correlation of pore sizes of different porous structures (MOF-808, UiO-66-NH_2, ZIF-8) on the catalytic performance of LnPOM-based composites in ODS studies.
CAT36 Photocatalytic oxidative coupling of amines by titanites perovskites.

EDUCACIÓN Y ENSEÑANZA DE LA QUÍMICA

Oral

EDU01 Utilización de metodologías activas para trabajar competencias transversales en asignaturas de Ciencias.

EDU02 Tres tristes tigres comen mijo en un mijal.

EDU03 Y nos dieron las diez y las once, las yodo, la una, las dos y las tres.

Póster/Panel

EDU04 Determinación de la dureza en las aguas. Ablandamiento de aguas por intercambio iónico.

EDU05 Práctica virtual de Laboratorio de Química: Determinación del calor de combustión y de formación de la aspirina (ácido acetilsalicílico).

EDU06 Caso Práctico: evaluación de la corrosión en armaduras de hormigón por medio de la medición del campo potencial.

QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Oral

IND01 Captura de CO_2 con carbones preparados a partir de serrín de pino (*Pinus radiata*)

IND02 Study and modeling of the equilibrium and dynamics of post-combustion CO_2 adsorption using carbon-based adsorbents.

IND03 Estudio físico-químico de sistemas de Triton X-102 + sales.

IND04 Viscosidad dinámica de sistemas binarios n-octano +1-alcohol.

IND05 Obtainment of different biosurfactant extracts from corn steep liquor depending on the extraction process.

IND06 Biodiesel production from residual cooking oils and its purification by adsorption processes based on adsorbents of natural origin.

IND07 Study of biodiesel production from waste cooking oil by ethyl transesterification and its purification using adsorption processes.

IND08 Identification of gramicidin in biosurfactant extract by ESI-MS: a preliminary study.

IND09 Antioxidant activity of biosurfactant extracts obtained from corn steep liquor.

IND10 Optimization of the hydrothermal extraction of antioxidants from Opuntia *ficus-indica.*

IND11 Valorization of liquid and solid extracts from Undaria pinnatifida using microwave assisted extraction.

IND12 Characterization of the Mediterranean green algae *Caulerpa prolifera* and investigation of its antioxidant capacity using green extraction assisted by microwaves.

IND13 Modeling and simulation of biomass pyrolysis processes.

Póster/Panel

IND14 Synthesis of activated carbons from food and wood industrial by-products and application for dyes removal.

IND15 Removal of the inert coating from waste printed circuit boards using NaOH solutions under autoclaving treatment.

IND16 Effect of Dialysis and Purification on Bioactivity of *Ascophyllum Nodosum* Seaweeds Extracts.

IND17 Sugars and short-chain oligogalacturonides production from lemon peels.

IND18 Effect of Method, Solvent and Liquid–Solid Ratio on Phlorotannins Extraction From *Ascophyllum Nodosum* Seaweeds.

IND19 Sequential production of oligogalacturonides and arabinooligosaccharides by autohydrolysis of sugar beet pulp.

IND20 How the addition of polyphenols from *Ascophyllum nodosum* seaweeds affects to corn starch gels rheology.

IND21 Adsorption of polyphenols extracted from *Ascophyllum nodosum* seaweeds on native corn starch and corn starch gel.

IND22 *Eucalyptus globulus* wood fractionation by organosolv processing.

IND23 One-pot fractionation of *Pinus pinaster* wood by biphasic delignification with butanol/water.

IND24 Concentration and purification of pectin extracts from sugar beet pulp using different ultrafiltration/diafiltration configurations.

IND25 Recovery of humic acids from mixed municipal waste compost with alkaline extraction.

IND26 Ecofriendly extraction of phenolic compounds from Galician hop (*Humulus lupulus* L.) leaves using deep eutectic solvents.

IND27 Selective fractionation of olive tree prunings using partially immiscible mixtures of water and alcohols.

IND28 Solubilization of hemicelluloses and lignin from Robinia wood via microwave-assisted autohydrolysis and delignification with deep eutectic solvents (DES).

IND29 BECCSU con captura de simulación de procesos hacia la sustentabilidad.

IND30 Optimizing spray drying conditions for green extracts from a commercial hop variety.

IND31 Bioactive Phenolic Compounds Extraction from Avocado Peels employing Deep Eutectic Solvents.

IND32 Potato peels waste as a sustainable source for biotechnological production of biofuels using very high gravity strategies.

IND33 Delignification of autohydrolyzed *Acacia dealbata* wood using carboxylic acid-based deep eutectic solvents (DESs).

IND34 Deslignificación de madeira de *Paulownia* utilizando disolventes eutécticos profundos.

IND35 Delignification assessment of vine shoots using deep eutectic solvents.

IND36 Ultrasound-assisted depolymerization of oligocarrageenan from *Mastocarpus stellatus.*

IND37 Valorization of CO2 to chemicals using iron carbides as catalyst.

IND38 How the addition of polyphenols from *Ascophyllum nodosum* seaweeds affects to corn starch gels rheology.

IND39 Determinación de la curva de Destilación ASTM D-86 de una gasolina comercial.

IND40 Ensayo mecánico de dobladura de un acero F-1120. Práctica de laboratorio.

IND41 Extração de aromas para o desenvolvimento de kits aromáticos associados ao vinho.

IND42 Potencialidad de la lignina en la mejora técnica y medioambiental de las carreteras.

NANOQUÍMICA Y NANOTECNOLOGÍA

Oral

NN01 Size and coating-dependent toxicity of silver nanoparticles to human monocytes and macrophages.

NN02 Electroactive porous frameworks based on redox-active organic building blocks for electronics applications.

NN03 New electrodes based on redox-active porous materials towards more efficient batteries.

NN04 Optimization of one-pot microwave synthesis of multicolored carbon dots.

NN05 WO_3_naphthopyran hybrid nanomaterials: the new frontier to accomplish enhanced light-responsive textiles.

NN06 Casein Micelles: Optimizing Encapsulation Towards Polyphenols Delivery.

NN07 Synthesis of TGA-capped CdTe quantum dots with controllable fluorescence wavelength.

NN08 Magnetic nanoparticles for removing rare earth elements from water.

NN09 Formulation of polymeric nanoparticles using a membrane fraction extract obtained by subcritical water extraction from *Laminaria ochroleuca* brown seaweed.

NN10 A new approach for assessing silver and titanium dioxide nanoparticles in tap water samples.

NN11 Dehydropeptide-Based Self-Assembled Hydrogels: *soft* nanostructured materials for the development of theranostic platforms.

NN12 Stimulus-responsive liposomes as a smart platform for prednisolone delivery to activated macrophages.

NN13 New Approaches for CO_2 Methanation in Ionic Liquid Systems.

NN14 Mitoxantrone-loaded lipid nanoparticles as a promising therapeutic strategy for breast cancer: two different functionalization strategies.

NN15 Advanced LIBS based on nanosilicon and lignocellulosic-based composites.

NN16 Searching for the chemistry that works: formulating hydrogels and nanogels towards atopic dermatitis therapy.

NN17 Biomass derived components to improve energy storage systems.

NN18 Characterization of κ- and ι- carrageenans-based hydrogels as potential vehicles in skin delivery.

NN19 Quantum dots and chemometrics: potential and advantages.

NN20 Verteporfin-loaded lipid nanoparticles as an effective approach for cancer photodynamic therapy.

<u>Póster/Panel</u>

NN21 New architectures in soft materials for combined cancer therapy: multifunctional dehydrodipeptide-based lipogels with magneto-plasmonic properties.

NN22 Self-assembly of bolaamphiphiles based on dehydropeptides.

NN23 Effect of Different Casein Removal Methods on the Purity and Yield of Milk-derived Exosomes.

NN24 Gold nanoparticles synthesized by natural photosensitizer hypericin.

NN25 Migration of cellulose nanocrystals from a PLA multilayer film functionalized by Ultrasonic Spray Coater.

NN26 Honey2KILL: antimicrobial Portuguese honey towards superbugs.

NN27 Multiple Lipid Nanoparticles loaded with essential oils as a new approach towards antimicrobial mastitis infection.

NN28 Naringin nano-delivery systems for inflammatory conditions.

NN29 The role of chemical modified SiO_2 nanoparticles in the tribological performance of a paraffinic oil.

NN30 Development of a Fluorescent Nanostructured Lipid Carrier (NLC) by a High-energy method.

NN31 New supramolecular hypergelators based on dehydroamino acid residues for biomedical applications.

NN32 Nanoplatforms drive slow down in skin ageing.

NN33 Nanolubricants stability: surface modification of nanoparticles.

NN34 Enhanced antioxidant activity of silver nanoparticles synthesized by *Codium tomentosum* aqueous extract.

QUÍMICA DE POLÍMEROS

Oral

POL01 Silylated poly(azomethine)s with possible applications in the optoelectronic field. Synthesis and characterization.

POL02 Cómo minimizar el rechazo de implantes empleando la química click.

QUÍMICA ANALÍTICA

Oral

QA01 Desenvolvemento dun marco analítico para a determinación de contaminantes orgánicos persistentes e móbiles en mostras de urina.

QA02 Optical sensors for amine vapours detection and discrimination.

QA03 Screening of organic micropollutants in mollusc and fish samples from the Portuguese coast by combining liquid and gas chromatography with high resolution mass spectrometry.

QA04 Desenvolvemento dun método para a determinación de biomarcadores do uso de cannabinoides mediante a análise de augas residuais con fins epidemiolóxicas.

QA05 Automatic on-line renewable micro-solid-phase extraction hyphenated to tandem mass spectrometry for the determination of uremic toxins in plasma.

QA06 Determination of acid lactase activity resorting to a high-throughput kinetic method.

QA07 Concanavalin A biosensor for evaluation of biopharmaceuticals.

QA08 Estudo do emprego de drogas ilícitas, alcohol e tabaco en España e Portugal durante a crise da COVID-19 en 2020 a través da análise de augas residuais con fins epidemiolóxicas.

QA09 Assessing the presence of organic micropollutants in surface water.

QA10 Immobilization of CYP3A4 on surface-modified electrodes: assessment of electroanalytical and electrocatalytic properties.

QA11 Valorização de espécies mediterrânicas subutilizadas: obtenção de óleo essencial com propriedades bioativas.

QA12 Semi-preparative separation and racemization study of MDPV enantiomers by liquid chromatography and absorption study on Caco-2 model.

QA13 Continuous flow bioconjugation of a fluorescent coumarin-lipid probe as a chemical reporter for membrane oxidation.

QA14 Determinação cinética do ácido acetilsalicílico usando pontos quânticos de CdTe e de $AgInS_2$ como sondas fluorescentes e U-PLS e ANN como ferramentas quimiométricas.

QA15	Development of a new mesofluidic platform to assess metal-based dihydrofolate reductase inhibitors.
QA16	Estudio fluorescente de la amina biógena Triptamina y su aminoácido precursor (Triptófano).
QA17	Validation of a method to quantify essential and potentially toxic elements in raw and cooked food matrices.
QA18	*In vitro* inhalation bioaccessibility estimation of atmospheric PM-associated organic compounds using simulated biological fluids.
QA19	Automatic identification of myeloperoxidase natural inhibitors in plant extracts.
QA20	As vantagens do uso da quimiometria na química analítica.
QA21	Low pressure chromatographic system with multiple pulse amperometric detection for multi-analyte determination in green coffee extracts.
QA22	Quantitative analysis of phosphopeptide enrichment methods.
QA23	Overcoming the seawater trace elements analysis challenge in a SPE-flow-based approach.
QA24	Finding biomarkers of ruminal acidosis through targeted and untargeted metabolomic analysis through *in vitro* rumen fermentation assays.
QA25	Renewable immunosensors based on lab-on-valve flow systems.
QA26	Detetores baseados em imagem: desenvolvimento e aplicação.

<u>Póster/Panel</u>

QA27	Polycyclic Aromatic Hydrocarbons Determination in Human Adipose Tissue.
QA28	Aplicaciones De La Microscopía RAMAN Confocal.
QA29	Paper-based analytical devices for instrumental and smartphone-based fluorimetric sensing of environmentally relevant inorganic species.
QA30	Development of a novel cost-effective method for the density separation of microplastics from marine sediments, followed by quantitative ^{1}H-nuclear magnetic resonance spectroscopy determination.
QA31	Determination of Sulfide in Waters by Smartphone-Based In-Drop Colorimetric Plasmonic Sensing involving hydrophobized PADs.
QA32	Occurrence and persistence of fungicides and insecticides in vineyard soils.
QA33	GC-MS screening method for the identification of semi-volatile compounds in bio-based and biodegradable food packaging materials.
QA34	Composição fenólica e atividade biológica de extratos de casca e ramos de *Juniperus communis* L. (zimbro comum).
QA35	Evaluación de la presencia de residuos de fungicidas e insecticidas en cerveza mediante cromatografía de líquidos y espectrometría de masas en tándem.

QA36 Direct, automated and sensitive determination of glyphosate and related anionic pesticides in environmental water samples using SPE on-line combined with LC-MS/MS.

QA37 Comprehensive characterization of volatile and semi-volatile compounds in e-liquids formulations for electronic cigarettes by gas chromatography accurate mass spectrometry.

QA38 Estudio espectrofluorimétrico del pesticida imidacloprid y su principal metabolito el ácido 6-cloronicotínico.

QA39 Time-Resolved Fluorescence Excitation-Emission spectroscopy and PARAFAC to solve overlapping signals.

QA40 Analytical Quality by Design for selecting optimal experimental conditions of a head space-solid phase microextraction for several phthalates analyzed by CG-MS.

QA41 Deseño de fase estacionaria para a separación de nanopartículas metálicas mediante cromatografía líquida.

QA42 Evaluation of agriculture plastics as vehicles of pesticides and concerning pollutants in the environment.

QA43 Single-cell-icp-ms measurements for studying silver nanoparticles internalization in cell lines from sea-bass and clams.

QA44 Statistical experimental design to determine phenolic compounds in seawater by the AgNPs synthesis.

QA45 Matrix solid-phase dispersion and ultrasound-assisted extraction in the extraction and polyphenolic characterisation from five varieties of brown algae.

QA46 Determinación de nanopartículas de dióxido de titanio en piensos empleados en acuicultura.

QA47 Revisión bibliográfica del empleo de reacciones fotoquímicas en electroanálisis.

QA48 Electrochemical evaluation of the psychoactive recreational drug 4-bromo-2,5-dimethoxyphenethylamine (2C-B).

QA49 Microencapsulation of benzyl isothiocyanate using β-cyclodextrins.

QA50 Determinación de medicamentos en aguas superficiales mediante inyección directa en cromatografía de líquidos acoplada a espectrometría de masas.

QA51 Firefighters' personal exposure to airborne polycyclic aromatic hydrocarbons during controlled forest fires.

QA52 O uso de uma sonda raciométrica combinando pontos quânticos de carbono e de $AgInS_2$ para a determinação de histamina recorrendo a modelos quimiométricos.

QA53 Potential inhibitory effect of new xanthones on acetylcholinesterase: an automatic assay.

QA54 Development of a microfluidic paper-based analytical device for the determination of iodide.

QA55 Characterization of *Achillea mellefolium* flower extracts as ingredients in organic cosmetics.

QA56 UPLC-MS lipidomic approach to evaluate potential biomarkers for the differentiation of HIV/HCV progressive stage.

QA57 Ion mobility spectrometry for the rapid and simultaneous analysis of three common analgesics

QA58 Partículas de caucho procedentes de ruedas de coche: determinación de agentes químicos relacionados con la mortalidad de especies acuáticas

QA59 Desenvolvemento dun método analítico baseado na extracción asistida por ultrasóns seguido de cromatografía líquida acoplada a espectrometría de masas en tándem para a determinación de herbicidas en solos.

QA60 Estimación del comportamiento en frío del biodiesel.

QA61 Dilución por biocombustible del aceite lubricante.

QA62 Evaluation of the Phenolic Content of Galician Honeys to Identify their Botanical Origin.

QA63 Electrochemical determination of cholecalciferol in water-ethanol mixtures using a glassy carbon electrode and unmodified screen-printed carbon electrodes.

QA64 Exploring the emission of volatile carbonyl compounds from wood-based panels by GDME and HPLC-DAD-MS/MS.

QUÍMICA FÍSICA

Oral

QF01 Development of Chemiluminescent Halogenated Coelenterazine Derivatives with Anticancer Potential.

QF02 Probucol – solvent effects on polymorph crystallization.

QF03 Active regulation of thermal transport using light-responsive molecular materials.

QF04 Understanding the physics of exchange of the alkaline metal on nitrate salts mixtures with ethylammonium nitrate.

QF05 β-Amyloid aggregation or phase separation induction by electrostatic interactions with small biomolecules.

QF06 Nanostructured Polythiophene Materials for Electrochromism.

QF07 New insight in 4th generation battery: Pure Ionic Liquid as functional quasi-solid electrolyte.

QF08 Flavylium-cucurbit[8]uril supramolecular polymers as photorheological fluids.

QF09 Alkylsilane and alkylsiloxane effect on the thermodynamics of ionic liquids.

QF10 Electrical Conductivity of Ionic liquids by Multi-frequency Impedance Methodolgy

QF11 Towards fine-tuning charge in vesicular drug delivery systems: role of spacer in cationic *gemini* surfactants at the air/water interface.
QF12 Environmental mobility of pesticides and agrochemical metabolites: volatility and phase transitions properties of some dichlorobenzonitrile isomers.

Póster/Panel

QF13 Localization and interaction of 3-hydroxy-4-pyridinone chelators with DMPC model membranes: A DSC and EPR Study.
QF14 The effects of DMSO on the thermal properties of DMPC liposomes.
QF15 Caracterización fotofísica da interacción do 6-amino-2-ciano-1,3-benzotiazol con proteínas amiloides e seroalbumina humana e bovina.
QF16 Thermal and photochemical reactions of n-pyridinechalcones (n = 2’, 3’, 4’).
QF17 *iSenseDSC*: a high precision microcalorimeter.
QF18 Exploring the effect of nanostructuration on the thermophysical properties of the 1-alkyl-3-methylimidazolium triflate series.
QF19 Extensive Study of the Electrical Conductivity of Imidazolium Ionic Liquids: the Anion Effect.
QF20 Energetic study of methyl-indanones with potential application in thermochemical processes.
QF21 Uso do intercalador Laranxa de tiazol para a detección e cuantificación de ADN de dobre febra.

QUÍMICA INORGÁNICA

Oral

QI01 Dinuclear copper(II) complexes as models for metalloenzymes.
QI02 Single ion magnets of macrocyclic N_5 and N_6 ligands.
QI03 Direct C-H arylation of dithiophene-tetrathiafulvalene: tunable electronic structure and 2D self-assembled molecular networks on surface.
QI04 Atmospheric carbon dioxide activation by a cobalt complex.
QI05 An efficient route to coinage metal mesocates.
QI06 A dysprosium field-induced single molecule magnet with a N_3O_2 flat donor.
QI07 Síntese, caracterización e estudo das propiedades biolóxicas de *E,Z*-[RuCl(η^6-*p*-cimeno)($\kappa^2 N3,S$-TSC)]$^+$ (TSC = tiosemicarbazona).
QI08 Au(III) π-Allyl Complexes: From Structure Analysis to Catalysis.

Póster/Panel

QI09 A metal-coordination-triggered carbamate hydrolysis process.
QI10 A magneto-structural study of a mononuclear dysprosium complex with a Schiff base N_6 donor.
QI11 Luminescent cyclometalated Pt^{IV} compounds bearing phenanthroline-based ligands with antiproliferative activity.
QI12 Obtaining an azine ligand via a thiocarbohydrazone desulfurization process.
QI13 Inorganic nanoparticles for the detection of circulating proteins associated with the response/resistance to neoadjuvant chemotherapy in HER2-positive breast cancer.
QI14 Silver nanoparticles for the detection of circulating serum protein biomarkers of non-muscle invasive bladder cancer.
QI15 Síntese de hidrocarburos iridaaromáticos policíclicos.
QI16 A new peroxo-complex of dysprosium with single-molecule magnet behaviour.
QI17 Synthesis of tridentate [*C, N, S*] iminophosphorane cyclometallated palladium compounds.
QI18 Active antitumoral thiosemicarbazone platinacycles.

QUÍMICA ORGÁNICA

Oral

QO01 Síntesis de nuevos sesquiterpen-polifenoles, actividad citotóxica y estudios de acoplamiento molecular inducido (*Docking*).
QO02 Síntese de análogos de nucleósidos e nucleótidos baseados em unidades de D-glucuronamida e contendo um anel 1,2,3-triazole potencialmente bioativos.
QO03 Nitrones' rearrangements: 7 WONDERS.
QO04 Multistate of chemical reactions of 7-diethylamino-4´-dimethylaminoflavylium. Thermodynamics, kinetics and Photochemistry modulated by water: ethanol, SDS and CTAB micelles.
QO05 Synthesis and anti-*Candida* Activity of Aminated Thioxanthones.
QO06 Chiral pool synthesis of new flavones with potential antitumor activity.
QO07 Influence of proton transfer on the luminescence of organic dyes.
QO08 Estrategia sintética para la obtención del primer análogo tipo Gemini del maxacalcitol.
QO09 Enhancing photophysical properties of BODIPYs through oxime and hydrazone functionalization: novel imaging agents.
QO10 Synthetic access to new indazole derivatives with promising anticancer features.
QO11 Polysaccharides from marine sources: synthesis of derivatives and tumor cell growth inhibition.

QO12 Synthesis of fumiquinazoline analogues with antibacterial, anti-biofilm and efflux pump inhibition potential.

QO13 Exploring the reactivity of a commercial diketopyrrolopyrrole.

QO14 New porphyrins for dye-sensitized solar cells.

QO15 Mild synthesis of nitrobenzenes from 3-formylchromones.

QO16 Ru(III) and Ir(III) complexes bearing porphyrin moieties: synthesis and photosensitizing activity against resistant melanoma cells.

QO17 Ohmic heating-assisted palladium-catalyzed cross-coupling reactions for the synthesis of *C*-glycosylquinolones.

QO18 Irá a inteligência artificial assumir o papel do Químico? Um estudo de caso com a reação carbonilativa de Suzuki.

QO19 Synthesis and characterization of porphyrins bearing electronic donating groups at *meso*-positions to be used as hole-transporting materials in perovskite solar cells.

QO20 Preparation of Open-Shell Polycyclic Conjugated Hydrocarbons based on Truxene

QO21 Towards the synthesis of large acenes, starphenes, and closely related structures

QO22 Synthesis of Soluble Trigonal Nanographenes by Pd-catalyzed Aryne Cyclotrimerization.

QO23 Synthesis of new porphyrin–fullerene conjugates for application in dye-sensitized solar cells.

QO24 α-Substituted 2-benzylchromones as monoamine oxidase inhibitors for the treatment of neurological disorders.

<u>Póster/Panel</u>

QO25 Larvicidal activity of the fungus *Penicillium sp.* 27 against *Culex quinquefasciatus.*

QO26 Photoredox transformations of Quinic Acid.

QO27 Synthesis and structure elucidation of metabolites of the synthetic cathinones pentedrone and methylone for further metabolism studies.

QO28 Discovery of new eugenol-azole hybrids as candidates of potent trypanocidal agents.

QO29 From the bottom of ocean to the lab: synthetic strategies of cyclic peptide marine-derived.

QO30 Curcumin-based molecular probes for fluorescence imaging of fungi.

QO31 New open-chain carbohydrate amides: synthesis, docking studies and acetylcholinesterase.

QO32 Synthetic access to new fused thiazoloindazole as acetylcholinesterase inhibitors: synthesis, characterization and molecular docking studies.

QO33 Synthesis of hexahydropyrroquinolines-2,3-diol, analogues of swainsonine, and prediction by molecular modeling of their inhibition power towards human Golgi a-mannosidase II.

QO34 New 4-aminoacridine-cinnamic acid conjugates as multi-stage antimalarial hits.

QO35 Docking-based Virtual Screening as a tool to identify new small molecules targeting SARS-CoV-2.

QO36 Preparation benzoporphyrin-based photosensitizers.

QO37 Synthesis of novel *C*-glycosyl flavonoids.

QO38 Metal Ion Sensors Based on Thiazolo[5,4-*d*]thiazoles.

QO39 Organocatalytic properties of the iminosugar DAB.

QO40 Expanding the Library of Cyclopentadienone Iron Tricarbonyl Complexes: Synthesis and Characterization of Novel Precatalysts.

QO41 Divergent syntheses of iminocyclohexitols and polydroxylated pipecolic acids.

QO42 Squaraine dyes derived from benz[*e*]indole as fluorescent probes for human serum albumin detection and quantification.

QO43 Study of the supramolecular self-assembly of Cu(II) complexes of pyridoxal derived ligands.

QUÍMICA Y SALUD

Oral

QS01 Mining the *Leishmania* Kinome.

QS02 O receptor da vitamina D como unha nova diana para o tratamento do cancro de mama.

QS03 The Reaction Mechanism of SARS-CoV-2 Spike Protein Cleavage by TMPRSS2: A Quantum Mechanics/Molecular Mechanics Study.

QS04 Melanostatin Aza-Peptides as Potent Allosteric Modulators of the Dopamine D_2 Receptors.

QS05 Discovery of Melanostatin-Based Potent Modulators of the Dopamine D_2 Receptors Using Furoic Acids as Proline Surrogates.

QS06 Uma Abordagem Bioisostérica na Descoberta de Potentes Análogos da Melanostatina Usando β-Aminoácidos.

QS07 Bio-guided optimization of *Cystoseira abies-marina* cosmeceuticals extraction by advanced technologies.

QS08 New synthetic cinnamic acid-flavone hybrids with promising photoprotective, anti-inflammatory and antioxidant activities.

QS09 New insights into the anti-inflammatory effects of 2-stryrylchromones.

QS10 Pyrroloquinolone-based hybrid compounds multitargeting the electron transport chain of *Mycobacterium tuberculosis.*

QS11 Recent advances in cancer therapies *via* carbon nanomaterials functionalized with porphyrins and analogues.

QS12 Anti-inflammatory activity of 2-styrylchromones in Human fibroblast like synoviocytes.

QS13 Urea derivatives of β-carboline indole alkaloids for reversing multidrug resistance in cancer.

QS14 Evaluation of the cytotoxicity effects of flavonol derivatives in human lung fibroblasts.

QS15 Active Pharmaceutical Ingredient's multicomponent solid forms: a contribution to enhance the trimethoprim biopharmaceutical performance.

QS16 Polyhydroxylated *bis*-chalcones: potential new inhibitors of cyclooxygenase 2.

QS17 Synthesis of naringenin sulfates and evaluation of their anti-inflammatory activity.

QS18 Cationic imidazolyl porphyrins bearing amphiphilic side chains combined with antimicrobials: new strategies to potentiate *E. coli* photodynamic inactivation.

QS19 Design of a disposable µPAD for on-hand quantification of urinary creatinine.

QS20 Development of Photoactive Materials for Photodynamic Therapy Based Applications.

QS21 Developing a computer-aided drug design approach to discover lead-like Phosphomannomutase 2 pharmaco-chaperones for congenital disorders of glycosylation (CDG) therapy.

QS22 New insights on the antimicrobial properties of amino-based flavylium dyes: promising candidates for photodynamic inactivation of bacteria.

QS23 Fluorinated contrast agents for application in ^{19}F MRI and PET.

QS24 New families of multi-target direct ligands for Alzheimer's Disease.

QS25 Estudo integrado da influência do tipo de cultivo e irrigação nas propriedades bioativas de *Cichorium spinosum* L.

QS26 Synthesis of di-imidazolyl porphyrins and their chlorin derivatives for photoinactivation of bacteria and viruses.

QS27 Improving benzisothiazolinone (BIT) effectiveness by cyclodextrin's encapsulation: Ecotoxicity and Antibacterial studies.

QS28 Peptide/ionic liquid-based therapeutics for the topical treatment of skin infections.

QS29 *Guiera senegalensis*: On the track of biofungicides development.

QS30 Unveiling membrane dependent mechanism of action of molecules with anticancer activity.

QS31 Water-soluble pyridinium-pyrazole phthalocyanines for photodynamic inactivation of Phage Phi6 as SARS-CoV-2 Model.
QS32 β-Phospholactams as a novel chemical tool to target serine hydrolases.
QS33 Synthesis, characterization and antibacterial profile of new GUMBOS.
QS34 Tricyclic compounds derivatives as new potential neuroprotective agents.
QS35 Development of new multitarget-directed ligands with potential application in alzheimer’s disease.
QS36 Following-up bladder cancer patient’s response to therapy.
QS37 High-resolution absolute quantitative proteomics revealed new immunohistochemical markers of oncocytic renal neoplasms.
QS38 The effect of varying the complexity of amines introduced into the squaric ring on the photobiological activity of aminosquaraine dyes.
QS39 Anti-proliferative effect of novel chlorophyll derivatives in breast cancer cell lines
QS40 The wound healing properties of starch-based photoactive materials.
QS41 Design, synthesis and evaluation of novel antileishmanial agents.
QS42 Synthesis and biological evaluation of acridine-triazine hybrids as acetylcholinesterase and butyrylcholinesterase inhibitors.
QS43 Silica nanomaterials based on ionic antimicrobial agents for infectious therapeutic diseases.
QS44 Conjugation of carbon nanomaterials with tetrapyrrolic macrocycles: Applications & challenges.
QS45 Porfirinas sulfonamidas como agentes fotossensibilizadores para inativação de bactérias multirresistentes
QS46 New hexadentate Fe chelator: an EPR study to access chelator interaction with liposome membrane models.
QS47 Pharmaceutical cocrystals: Design approaches.
QS48 Cytotoxicity induced by 3’,4’,7-trihydroxyflavone derivatives in *in vitro* models of osteosarcoma.
QS49 Can infrared analysis of blood plasma assist diagnosis of respiratory viral infection

Póster/Panel

QS50 Synthesis, characterization and evaluation of the cytotoxic activity against A549 cell line of 2,6-diformyl-4-methylphenol hydrazones.
QS51 Synthesis, characterization and DNA binding of a vanadium (V) complex derived from 2,6-diformyl-4-methylphenol.
QS52 Estudos sobre a síntese de novos heterociclos baseados na unidade de cromeno e purina.
QS53 Fighting bacterial infections: antimicrobial peptides and ionic liquids.

QS54 Study of new derivatives based on coelenterazine for photodynamic therapy.

QS55 Discovery of Neuroprotective Hits Using 2-Azanorbornane as a Constrained Proline Surrogate in Glypromate Neuropeptide.

QS56 Design, Synthesis, and Biological Evaluation of Glypromate-Based Neuroprotective Conjugates with Pharmaceutical Active Ingredients.

QS57 Fluoroquinolone metalloantibiotics: fighting *Staphylococcus aureus* infections.

QS58 BDDE, a marine bioactive metabolite, as inspiration for the synthesis of chalcone derivatives to fight antimicrobial resistance.

QS59 Point-of-care determination of calcium in saliva using a developed microfluidic paper-based analytical device.

QS60 Cromeno[2,3-*b*]piridinas: síntese e avaliação do potencial anticancerígeno para o cancro da mama.

QS61 Indoor levels of fine and ultrafine particles at Portuguese fire stations.

QS62 Towards the “greenness” of a chemical synthesis of a new antifouling compound.

QS63 Synthesis of new surface-active ionic liquids derived from antimalarial drugs and bile acids.

QS64 Synthetic triazole compounds as potential inhibitors of SARS-CoV-2 attachment into host cells.

QS65 *Synthesis* and *in vitro* evaluation *of versatile cell-penetrating* mitochondriotropic antioxidants.

QS66 Tailoring VAS2870 scaffold to develop new covalent NOX2 inhibitors.

QS67 Fiscalins: a new source of substance P antagonists?.

QS68 Beyond chemical bonds.

QS69 Bladder Cancer: The Future of Diagnostic and Patient Monitoring.

QS70 Development of a Robust Ultrasonic-Based Sample Treatment to Unravel the Proteome of OCT-Embedded Solid Tumor Biopsies.

QS71 Biotin-bearing squaraine dyes as potential antitumor photodynamic agents: an *in vitro* preliminar study.

QS72 How the selectivity of Zn(II) ligands towards G4 DNA structures is influenced by the number and position of the positive charges.

QS73 Low serum bromine levels in chronic hemodialysis patients – is there any clinical impact? .

QS74 Trace element imbalances in hemodialysis patients: new data from a cohort of Portuguese patients.

QS75 Association between natural exposure to lithium and suicide rate: an ecological and human biomonitoring study in northern Portugal.

QS76 Reference intervals for whole blood trace elements in the Angolan adult population.

QS77 The effect of repeated blood donation on whole blood trace element status – a cross-sectional study in Angolan donors.

QS78 Synthesis of new purine nucleosides as potential biometal chelators and cholinesterase inhibitors.

QS79 New halogen hydrazones derived from pyridoxal and their biological behavior.

QS80 Benz[*e*]indole and indolenine squaraine dyes derivatives as antifungal agents and fluorescent probes.

QS81 Exploring the bioactive potential of *Artemisia annua* L. hydroethanolic extracts obtained by microwave-assisted extraction.

QS82 Development of a pH-sensitive dressing for clinical monitoring of chronic wounds.

QUÍMICA TEÓRICA

Oral

QT01 Interface between BmimPF$_6$ ionic liquid and gold metal surface from MD simulations perspective.

QT02 The Reaction Mechanism of SARS-CoV-2 Spike Protein Cleavage by TMPRSS2: A Quantum Mechanics/Molecular Mechanics Study.

QT03 (Non)-Polarizable models for magnetic ionic liquids.

QT04 Interface between BmimPF$_6$ ionic liquid and gold metal surface from MD simulations perspective.

QT05 Composición lipídica alterada provocada por COVID en fase aguda y persistente y la influencia del sistema inmune innato: Un estudio de Dinámica Molecular.

QT06 Back to the Chirality in Coarse-Grained Cyclic Peptides: The Ma(R/S)tini parametrization.

QT07 Exploring innate immune system peptides and their cell membrane interaction.

Póster/Panel

QT08 Study of Sodium Hexanoate and Dodecanoate Salt-Based Eutectic Solvents by Molecular Dynamics Simulation Approach.

CONFERENCIAS PLENARIAS

APERTURA

The Critical Role of Energy Storage in the Electric Economy and Overcoming Climate Change

M. Stanley Whittingham
Chemistry Department, Binghamton University, Binghamton, NY 13850

The Nobel committee stated in awarding the 2019 Chemistry Nobel Prize to John Goodenough, Akira Yoshino and myself "They have laid the **foundation** of a wireless, **fossil fuel-free society**, and are of the greatest benefit to humankind." It is now time for all of us to take action.

Energy storage, and in particular electrochemically-based storage, is critical in enabling the electric economy, just as it was for enabling the communications revolution. Lithium batteries have played the key role to date, but electrochemistry is also essential to the success of a clean hydrogen economy and to the attainment of a cleaner mining industry, one that would be based on electro-reduction rather than carbothermal processes.

Electric transportation, whether automobiles or tramcars/trolly buses, was dominant at the beginning of the last century. However, the discovery of oil changed all that. It was not until the 1970s that Exxon and then the US Department of Energy embarked on major battery initiatives to re-electrify transportation. That effort led to the critical role of intercalation reactions and the development of the lithium-ion battery and the use initially by SONY in Japan to miniaturize electronic music devices, and then by Apple bringing instant communication to the world and obsoleting land-line phones and the telegraph.

Today, the demand for electric vehicles far surpasses the supply despite their high cost. The other major demand for Li batteries is to enable renewable energy and to make the grid more resilient. In order to address these needs, we researchers need to find new materials to make the next generation batteries that are lower cost, have a secure supply chain and are safer. Can we make batteries with the desired properties using the most abundant redox active metals like iron, manganese and vanadium? Can we make batteries that will last essentially forever; these could be used for electric vehicles that are connected to the grid at all times when not actually moving. I will discuss some of the recent research trends that address these challenges, and the opportunities for chemists.

Hydroxypyridinones: Chelators to Life Sciences

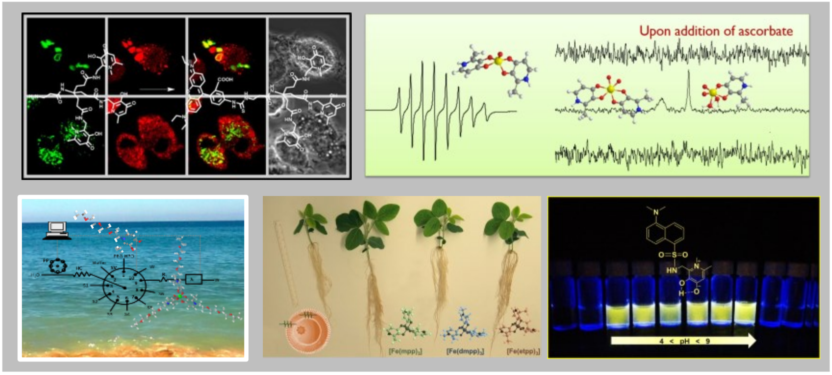
Maria Rangel[1,*]

[1] REQUIMTE-LAQV, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto
4050-313 PORTO, PORTUGAL
**mrangel@icbas.up.pt; www.chel2life.org*

Chelators of the 3-hydroxy-4-pyridinone class are known for their chemical, biomedical, agricultural and environmental applications. The possibility of using the ligands in such a variety of fields is mainly due to their high affinity towards M(II) and M(III) metal ions as well as their versatility in synthesis.

A significant number of bidentate ligands with variable lipophilicity has been prepared and used to produce polydentate ligands. Also, additional functionalities such as fluorophores and anchoring molecules to connect the ligand units to particular molecular frameworks have been successfully introduced thus enlarging their range of application. Metal ion chelates with 3-hydroxy-4-pyridinone ligands have also found application as metallodrugs and micronutrient fertilizers.

An overview of the work developed in the ***chel2life laboratory*** and regarding the design of ligands and complexes, the study of their chemical properties, their affinity towards biological membranes and biological activity will be presented. Particular attention will be given to the design of molecules to be tested in (a) novel therapeutic strategies such as, Infection and Diabetes Mellitus (b) Metal Ion Sensing and (c) Plant Nutrition.



Agradecimientos

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Aryne Chemistry in the Graphene Era

Dolores Pérez

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS),
Universidade de Santiago de Compostela, Santiago de Compostela, Spain
dolores.perez@usc.es

The discovery of graphene and other carbon-based materials has opened a new era in materials science, an era in which synthetic organic chemistry is called to play a very important role. In particular, the tailored, bottom-up synthesis of nanosized graphene substructures (*nanographenes*) and large polycyclic aromatic hydrocarbons (PAHs), with customized shapes and electronic properties, is currently a very active area of research. In this context, aryne intermediates are ideal synthetic building blocks, providing privileged strategies for the convergent construction of polycyclic compounds containing aromatic rings.

In this lecture, some recent contributions from our group to this field will be presented,[1,2] with particular emphasis on the use of polycyclic arynes and bisaryne precursors for the straightforward access to extended and/or structurally complex aromatic architectures. Our efforts towards the synthesis of singular aromatics and relevant π-functional materials, such as acenes, cycloarenes, porous nanographenes or novel fullerene derivatives, will be included. Some results from our fruitful collaborations with surface physicists, which allow the imaging and manipulation of our compounds at the single-molecule level by SPM techniques, will also be highlighted.

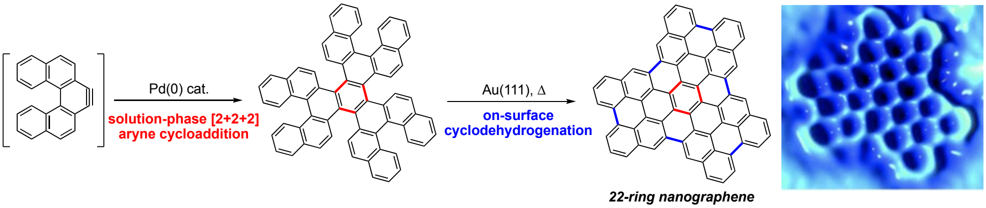

Fig. 1. Synthesis and single molecule imaging of a 22-ring nanographene, by combination of *solution-phase* Pd-catalyzed aryne cyclotrimerization and *on-surface* six-fold cyclodehydrogenation [3].

Aknowledgments

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Determination of microplastics in environmental samples

José M. Andrade-Garda

Grupo de Química Analítica Aplicada.
Departamento de Química. Campus da Zapateira
Universidade da Coruña, A Coruña, 15071, A Coruña, Spain.
andrade@udc.es

It is possible to set the decade after the second World War as the generalized onset of the 'plastic era'. Despite several plastics had been commercialized before that, the portfolio of massive production of plastics can be traced back to then. They appeared as a very convenient and economically-affordable commodity to address many Societal challenges at that moment: they avoided the use of limited resources and showed excellent properties, like durability, flexibility, an immense variety of applications, low weight but high resistance, quite affordable customization for different customers, etc. To sum up, plastics were considered like a step forward in the development of Society.

Curiously, many of those advantageous properties, combined with a general looseness of humans towards correct waste management, ended up in the generation of the problem that nowadays all the Earth ecosystems suffer: the presence of huge amount of plastics residues. Many spectacular images have shown animals trapped in macroplastics (or big fragments of plastics in their stomachs when corpses are find in beaches), but further than that the entrance of small microplastics (mostly in the nano scale) on the food web is being observed already. So concern arose on citizens and politicians, who are pushed to take actions. Althought this is far from simple because of the lack of knowledge (many times, lack of comparability) on the abundance, behaviour, fate and sinks of microplastics (MPs). Further, their effects on the biota are not still clear.

In this lecture some relevant aspects for the determination of microplastics (MPs) in environmental matrices are reviewed. Special emphasis will be placed on two major issues, namely:

1. Sample treatment. This is usually a very lengthy step and it determines the –commonly- very low overall sample throughput, ca. 15 days in many cases. Besides, care should be taken on the reagents used to get rid of the sample matrix as they might degrade the small polymer particles.
2. Chemical characterization of the particles: in order to quantify and classify the microplastic particles according to the major polymer constituting them. In particular, attention will be devoted to infrared measurements as they are a common workhorse nowadays to cope with this issue. However, different IR techniques can be possible and a general review of them will be posed.

Finally, some general recommendations will be given for reporting the results as there is an overwhelming disparity in literature and this hampers the possibility of comparing results. Indeed, this problem has been put forward by many international organizations as it difficults decision-making.

Prescriptomics

José Luis Capelo Martinez

Department of Chemistry. Faculty of Science and Technology. NOVA University of Lisbon. Portugal.
jlcm@fct.unl.pt

Analysis of proteins has been an integral part of clinical chemistry for decades. However, technological advances have opened new opportunities for the large-scale analysis of proteins for clinical diagnostic purposes and personalised medicine.

First, the development of mass spectrometers with significantly higher resolution and more extensive dynamic range has allowed generating of high-quality quantitative data from complex sample matrices such as serum, plasma, urine, and tissue biopsies without the need for isotopic labelling. Instruments like TOF, Orbitrap, FT-ICR and the most recent timsTOF were a stepping-stone towards proteomic-based personalised medicine by facilitating the detection of patient-specific protein signatures that reorganise over time due to genetic, environmental, and treatment constraints.

Second, developing high-throughput robust chromatographic-based sample preparation methods in conjunction with mass spectrometry has allowed the processing of many clinical specimens such as serum, urine, cerebrospinal fluid, and tissue biopsies in an efficient and reproducible manner [6]. Parallel to such achievements, the exciting advances done by bioinformatics have been a cornerstone in translating quantitative proteomics data into actionable clinical information.

We are what our genetic code express. And what we express can now be quantified. By quantifying the proteome expressed by a patient, any disease can be diagnosed, prognosed and followed either using a solid or a liquid biopsy.

Within this talk, I will introduce the analytical chemistry-driven concept of prescriptomics by describing how the advances in sample treatment, mass spectrometry, chromatography and bioinformatics have led to the advent of truly personalised medical treatment.

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COMUNICACIONES ORALES

QUÍMICA ALIMENTARIA

Desenvolvimento de um novo vinagre espirituoso de origem vínica

Cristina Laranjeira[1],[*], Marco Alves[2], Helena Mira[1], Isabel Torgal[1],Tânia Orvalho[2], Maria Lima[1], Sara Canas[3], Ilda Caldeira[3]

[1]Instituto Politécnico de Santarém - ESAS, Quinta do Galinheiro, 2001-904 Santarém, Portugal
[2]INOV'Linea-TagusValley, Rua José Dias Simão, 2200-062 Abrantes, Portugal
[3]Instituto Nacional de Investigação Agrária e Veterinária, 2565-191 Dois Portos, Portugal
**cristina.laranjeira@esa.ipsantarem.pt*

O vinagre é um produto com tradições milenares. Muito enraizado nas culturas gastronómicas mediterrânica, atlântica e asiática, a sua definição não é consensual, internacionalmente; contudo, na UE, "vinagre" obtém-se exclusivamente por dupla fermentação alcoólica e acética de substâncias de origem agrícola (EN 13188:2000). A sua produção é um exemplo clássico de sustentabilidade no uso de recursos sub-aproveitados, posicionando-se no fim da fileira de transformação agroalimentar. Recentemente, a valorização dietética deste género alimentício hipocalórico e funcional, influenciada também pela *Nouvelle Cuisine* e por preocupações com a alimentação na saúde, tem-se traduzido numa maior diferenciação e prestígio do produto e na procura de novos produtos vinagreiros [1,2].

Na linha *Agrio* do projeto *AgetEm* (POCI-01-0145-FEDER-023583) desenvolveu-se um novo protótipo de vinagre espirituoso (2017-2020), por acetificação de destilado vínico, monovarietal, produzido por vinificação de uvas brancas da casta Tália da Coleção Ampelográfica Nacional (Portugal). A tecnologia deste novo vinagre espirituoso compreende três fases: vinificação, destilação intermédia em alambique e acetificação em cultura submergida, usando como acetificador, um fermentador de laboratório (CSTR) com agitação e arejamento contínuos. A inoculação do destilado vínico foi realizada com "vinagre-mãe": vinagre de vinho branco bruto, recolhido num acetificador industrial em laboração, que veiculou a cultura viva de bacterias acéticas e garantiu a acidez necessária ao arranque e manutenção da fermentação acética. Temperatura e volume da mistura no acetificador, condições de arejamento e agitação, pH, acidez total e concentrações de etanol e total (GK) foram controladas [3]. Do vinagre espirituoso obtido nos ciclos de arranque e adaptação, fizeram-se seis lotes, que foram analisados por cromatografía GC-FID [4] e HPLC [5]. Os lotes apresentaram o mesmo espectro de compostos presentes no vinho e no vinagre vínico (modificados pela destilação e pela acetificação), mas obtiveram-se perfis distintos, com diferenças significativas nos teores de compostos voláteis maioritários e ácidos orgânicos quantificados. O ácido acético – responsável pelo sabor *sui generis* do vinagre - é quantitativamente o composto mais importante, como seria espectável. As análises de variância simples (ANOVA) e multidimensional (ACP, *clusters*) à matriz de resultados, indicaram que os ácidos D-glucónico, tartárico e succínico, bem como os compostos voláteis acetato de etilo, 2-feniletanol e glicerol, contribuíram para uma maior diferenciação entre os lotes de vinagre.

O protótipo do novo vinagre espirituoso, além de ácido acético, acetoína e etanol residual - compostos cuja presença conjunta é necessária para assegurar a genuinidade enquanto produto obtido de dupla fermentação alcoólica e acética [1] - contém outros compostos secundários relevantes na definição do seu perfil de composição, nas características organoléticas e como garantia de autenticidade. Inovador e conveniente – com longa vida útil e múltiplas aplicações alimentares - a sua tecnología é sustentável, possibilitando o aproveitamento de excedentes estruturais de vinho, destilados vínicos ou aguardentes e assegurando também as boas práticas vinagreiras e a segurança alimentar.

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Mycotoxins and inorganic arsenic in rice: the Portuguese scenario and human risk assessment in the worldwide context

Liliana J.G. Silva[1,*], **André M.PT. Pereira**[1], **Inês Pedro**[1], **Catarina Perdigão**[1], **Alexandra Silva**[1], **Inês Encarnação**[1], **Sofia Duarte**[1,2], **Anabela Almeida**[2,3], **Angelina Pena**[1]

[1]LAQV, REQUIMTE, Laboratory of Bromatology and Pharmacognosy, Faculty of Pharmacy, University of Coimbra, Polo III, Azinhaga de Stª Comba, 3000-548 Coimbra, Portugal
[2]Department of Veterinary Sciences, Vasco da Gama Research Center, Vasco da Gama University School, 3020-210, Coimbra, Portugal
[3]CIBIT - Coimbra Institute for Biomedical Imaging and Translational Research, University of Coimbra, 3000-548, Coimbra, Portugal
**ljgsilva@ff.uc.pt*

Rice is the second most important cereal crop and an essential component of the diets and livelihoods of billions of people, including infants and celiac patients [1]. In a time of concern about world hunger, impact of climate change, population growth and future food security, rice production is threatened, as well as both, the quantity and the quality of rice that is available for consumption [2]. This can also enhance human exposure to chemical hazards, such as mycotoxins and metalloids.

The goal of this study was firstly to evaluate the occurrence of aflatoxin B1 (AFB1), ochratoxin A (OTA), zearalenone (ZEN) and inorganic arsenic (InAs) in rice, evaluating the Portuguese scenario in the worldwide context and the Portuguese population exposure. Rice intended for human consumption was commercially acquired and provided by Portuguese rice producers. The determination of every mycotoxin involved competitive enzyme immunoassays (ELISA), with limits of detection (LODs) of 0.8, 1 and 1.75 µg/kg, for OTA, AFB1 and ZEN, respectively. InAs analysis was achieved by inductively coupled plasma mass spectrometry (ICP-MS), with a LOD of 3.3 µg/kg.

From the 36 samples analysed, none showed contamination by OTA. AFB1 was present in 2 (4.8%) commercially acquired branded samples, in levels of 1.96 and 2.20 µg/kg, of white short rice and of wild long rice, respectively. These levels exceeded the European maximum permitted level (MPL) of 1 µg/kg. Concerning ZEN, 88.89% of the total samples showed levels above the LOD, up to 14.25 µg/kg (average of 2.75 µg/kg). Significant difference was found between private and white label samples (p=0,0196), with white label samples presenting higher values. Regarding InAs, 100% of the samples showed levels above the LOD, up to 100.0 µg/kg (average of 35.3 µg/kg), none exceeding the MPL (200 µg/kg). The lowest p value, <0.0001, was obtained between brown and white rice, with brown presenting higher values. No correlation was found between mycotoxin and InAs contamination.

Regarding AFB1 exposure, for every population studied, the maximum estimated daily intake (EDI) value was of 5.79 ng/kg bw/day. Children presented the higher risk values, followed by adolescents and adults, both considering the provisional maximum tolerable daily intake (PMTDI) (1 ng/kg bw/day) proposed by Kuiper-Goodman [3] and the margin of exposure (MOE) approach (170 ng/kg bw/day) [4]. As for ZEN, the maximum EDI was of 77.81 ng/kg bw/day, for the worst case scenario and the 95th consumption. Again, children presented the higher risk values considering the tolerable daily intake (TDI) value of 250 ng/kg bw/day. For InAs, the maximum EDI value was 0.5463 µg/kg bw/day, also obtained for children, once again, the group with higher risk values. The MOE increased when the 95th consumption percentile was considered, to values lower or close to 1.

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Inhibición de la actividad microbiana y la alteración lipídica en productos marinos mediante empleo de extractos de la macroalga *Bifurcaria bifurcata*

Santiago P. Aubourg[1,*], **José M. Miranda**[2], **Marcos Trigo**[1] **y Jorge Barros-Velázquez**[2]

[1]Departamento de Ciencia y Tecnología de Alimentos, Instituto de Investigaciones Marinas (CSIC), Vigo, España
[2]Departamento de Química Analítica, Nutrición y Bromatología. Escuela de Ciencias Veterinarias, Universidad de Santiago de Compostela, Lugo, España
** saubourg@iim.csic.es*

Las algas marinas forman parte de la dieta humana en algunos países asiáticos desde la antigüedad. Recientemente, su uso está recibiendo un creciente interés en el mundo occidental debido a sus excelentes propiedades nutricionales, así como por su aporte en componentes con propiedades antimicrobianas, antioxidantes, antiinflamatorias y antitumorales [1,2]. Entre estas algas, *Bifurcaria bifurcata* destaca por su abundancia en las costas atlánticas de Portugal, Francia y España [3] así como por sus propiedades conservantes demostradas en diversos experimentos *in vitro* [4].

Este estudio se centra en la utilización de esta macroalga parda al objeto de mejorar la calidad de pescado comercializado en estados fresco y enlatado. Para ello, se utilizaron disoluciones acuosas de extractos de dicha alga para la elaboración del hielo utilizado como medio de conservación en refrigeración de gallo (*Lepidorhombus whiffiagonis*); los efectos de los extractos del alga sobre el desarrollo de la actividad microbiana y la alteración lipídica fueron analizados durante un periodo de conservación de 14 días. Por otra parte, los extractos de *B. bifurcata* fueron incluidos en el medio de cobertura empleado durante el enlatado de caballa atlántica (*Scomber scombrus*); después de tres meses de conservación del producto enlatado, se analizaron los efectos originados sobre la calidad del pescado.

En lo que respecta al estudio de gallo refrigerado, se observó un marcado efecto inhibidor en el desarrollo de distintos grupos microbianos (aerobios, psicrótrofos, Enterobacterias, proteolíticos y lipolíticos), así como en la formación de ácidos grasos libres y compuestos fluorescentes. Por su parte, el experimento de enlatado de caballa reflejó un efecto inhibidor por parte del extracto de alga sobre la formación de compuestos fluorescentes y sobre el incremento de los parámetros L^* y b^* de color. Se concluye que ambas estrategias (inclusión en el hielo de refrigeración y en el medio de cobertura del enlatado) pueden significar un importante avance a la hora de retener la calidad de pescado fresco y enlatado, respectivamente.

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Diferenciación quimiométrica de tequilas blancos en función de sus espectros infrarrojos

Diego Vieites Millán (*), José Manuel Andrade Garda

Universidade da Coruña, Campus da Zapateira, 15008, A Coruña, España.
(*) *diego.vieites@udc.es*

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En este trabajo se abordó el estudio quimiométrico de espectros de la zona infrarroja media pertenecientes a 134 bebidas alcohólicas comerciales mexicanas derivadas del agave. El objetivo principal fue evaluar si se podían observar diferencias entre distintas clases de productos comerciales: destilados, licores y tequilas provenientes de diversas marcas comerciales de origen mexicano. En concreto, se aplicaron dos técnicas de minería de datos: Análisis de Componentes Principales y Análisis Cluster (o Análisis jerárquico de Conglomerados).

Las principales conclusiones fueron:

1. Es posible diferenciar entre las muestras de tequila comercial y las de destilados y licores (región 1770 cm^{-1} y 1485 cm^{-1}, datos autoescalados, subespacio PC1-PC2-PC3). Mediante PCA dinámico se pudo reducir la zona de interés al rango 1717 - 1490 cm^{-1}.
2. Se pudo diferenciar entre tequilas blancos y tequilas jóvenes (físicamente tienen la misma apariencia). No obstante, la diferenciación no fue total. Para ello se necesitó el subespacio PC1-PC3 (4000 - 401 cm^{-1}; sin escalado). Usando PCA dinámico se pudo reducir el número de números de onda a las regiones siguientes: 3667 - 3653, 3644 - 3637, 2988 - 2960, 2911 - 2709, 1466 - 1448, 893 - 892 y 872 - 861 cm^{-1} (en total, 295 números de onda).
3. No fue posible diferenciar los tequilas añejos y extra-añejos, probablemente por la variabilidad espectral que generan los procesos de envejecimiento en barricas de roble.

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Plantas condimentares do género *Thymus* como uma alternativa natural para conservação de alimentos

Eleomar Pires Jr[1,2,3], Tatiane Oliveira[1,2], Eliana Pereira[1,2], Maria Inês Días[1,2], Ricardo Calhelha[1,2], Marina Kostić[4], Marina Sokovic[4], Miguel Prieto[3], I.C.F.R Ferreira[1,2], Cristina Caleja[1,2*], Lillian Barros[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, C. Santa Apolónia, 5300-253 Bragança, Portugal.
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[3] Grupo de Nutrição e Bromatologia, Departamento de Química Analítica e Alimentar, Faculdade de Ciência e Tecnologia de Alimentos, Universidade de Vigo, C. Ourense, E-32004 Ourense, Espanha.
[4] Institute for Biological Research "Siniša Stanković" - National Institute of the Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia
**e-mail de contacto: ccaleja@ipb.pt*

A indústria alimentar tem vindo a ser desafiada no sentido de impulsionar a inovação nos conservantes alimentares, principalmente devido à resistência dos consumidores em relação à utilização de aditivos artificiais [1]. O género *Thymus* é constituído por aproximadamente 350 espécies distribuídas por todo o mundo [2]. Estas são tradicionalmente usadas como plantas condimentares e medicinais, destacando-se como fontes promissoras de ingredientes bioativos naturais [3]. O presente estudo pretendeu caracterizar a composição fenólica e avaliar as propriedades bioativas de duas espécies de *Thymus* (*T. mastichina* L. e *T. pulegioides* L.) de forma a comprovar o uso potencial como ingrediente conservante natural na indústria alimentar. Os extratos hidroetanólicos (EtOH/H_2O - 80:20, *v/v*) de *T. mastichina* (ETM) e *T. pulegioides* L. (ETP) foram obtidos através de extração assistida por calor. Os compostos fenólicos foram identificados e quantificados por HPLC-DAD-ESI/MS, onde o ETP revelou a presença de catorze compostos fenólicos destacando-se o kaempferol como o composto maioritário; e, por sua vez, o ETM revelou a presença de doze compostos sendo o ácido rosmarínico o maioritário. A atividade antioxidante foi avaliada através de quatro ensaios *in vitro*: capacidade bloqueadora de radicais livres, poder redutor, inibição de peroxidação lipídica e inibição da hemólise oxidativa. A atividade citotóxica foi avaliada em linhas celulares tumorais humanas (carcinoma da mama, pulmão e gástrico e adenocarcinoma colorretal) e não tumorais (linha primária de fígado de porco, linha celular de rim de macaco), utilizando o método da sulforodamina B. A atividade anti-inflamatória foi testada usando uma linha de macrófagos de rato pela capacidade de inibir a produção de NO. Por fim, a atividade antimicrobiana foi avaliada usando um painel de seis bactérias e seis fungos selecionados segundo a sua importância a nível de saúde pública. Os resultados demostraram que ambos os extratos apresentaram desempenho bioativo promissor, sem apresentar toxicidade até à concentração máxima testada (GI_{50} > 400 µg/mL). O ETM apresentou melhor potencial antioxidante e antimicrobiano, enquanto o ETP se destacou pelo melhor potencial citotóxico. A composição em compostos fenólicos poderá justificar o desempenho bioativo dos extratos analisados. Desta forma, é possível afirmar que plantas do género *Thymus* surgem como alternativas naturais para a obtenção de extratos bioativos com potencial de aplicação na indústria alimentar como conservantes naturais.

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ALM06

Caracterização dos resíduos de *Brassica oleracea* L. para obtenção de um potencial ingrediente natural

Ana Luisa Pepinelli[1,2,3], Tatiane Oliveira[1,2,4], Eleomar Pires Jr[1,2], Cristina Caleja[1,2], Maria Inês Días[1,2], Marina Kostić[5], Marina Sokovic[5], Ricardo Calhelha[1,2], Filipa Mandim[1,2], Odinei Gonçalves[3], Maria Beatriz Oliveira[4], Eliana Pereira[1,2], Lillian Barros[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, C. Santa Apolónia, 5300-253 Bragança, Portugal.
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[3] Universidade Tecnológica Federal do Paraná, Câmpus Campo Mourão, Campo Mourão, Paraná, Brasil.
[4] REQUIMTE/LAQV, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[5] Institute for Biological Research "Siniša Stanković"- National Institute of Republic of Serbia, University of Belgrade, Boulevard Despota Stefana 142, 11000 Belgrade, Serbia.
** e-mail de contacto: eliana@ipb.pt*

A comunidade cientifica, em parceria com a indústria alimentar, tem vindo a estudar diferentes matrizes naturais, a fim de obter ingredientes funcionais com potencial aplicação neste setor industrial. Nesse sentido, este trabalho pretendeu fazer a caracterização de *Brassica oleracea* var. Acephala (popularmente conhecida como couve galega) quanto ao seu perfil fenólico e ação biológica, com o objetivo de identificar compostos fenólicos com potencial conservante e/ou bioativo para incorporação na indústria alimentar. O perfil fenólico individual foi obtido através de um sistema de HPLC-DAD/ESI-MSn e o potencial bioativo foi avaliado através de ensaios *in vitro*. A atividade citotóxica foi avaliada em linhas celulares tumorais humanas (AGS, CaCo2, MCF-7, NCI-H460) e a toxicidade em uma linha celular não tumoral (VERO), através do método colorimétrico da sulforodamina B. A atividade anti-inflamatória foi estudada em macrófagos de rato (RAW 264.7); a atividade antimicrobiana foi testada usando o método de microdiluição; e a atividade antioxidante foi avaliada através dos ensaios de TBARS (inibição da peroxidação lipidica) e CAA (atividade antioxidante celular). O perfil fenólico dos bioresíduos de couve galega revelou a presença de moléculas com elevado interesse em concentrações promissoras. Em relação ao potencial bioativo da amostra, foi possível observar uma interessante atividade antioxidante pela análise de TBARS, onde na concentração de 19 µg/mL foi possível oferecer 50% da atividade, porém pela análise de CAA os resultados foram moderados, com uma concentração de 2000 µg/mL com uma inibição de 40%. A atividade antimicrobiana revelou resultados muito satisfatórios, destacando-se as bactérias *Bacillus cereus* e *Enterobacter cloacae* e os fungos *Aspergillus fumigatus* e *Penicillium fumiculosum* como as estirpes mais suscetíveis ao efeito do extrato da couve. Em relação à atividade citotóxica e anti-inflamatória, o extrato da couve não apresentou capacidade antiproliferativa na concentração máxima testada (400 µg/mL), revelando a ausência de potencial antitumoral e anti-inflamatório, mas também, provando a ausência de toxicidade do extrato. Considerando esses resultados, os bioresíduos da couve apresentam uma composição rica em compostos de elevado interesse, nomeadamente com potencial antioxidante, o que pode ser interessante para o desenvolvimento de ingredientes funcionais com possíveis aplicação na indústria. Para além disso, a reutilização de subprodutos permitirá não só diminuir o desperdício alimentar, como também criar soluções estratégicas no setor agroindustrial de crescimento económico e sustentabilidade.

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Caracterización detallada de la harina del mesocarpio de *Attalea speciosa* y su aplicación para el desarrollo de nuevos productos de panadería

Souza MVS,[1,2,3] Saldanha A,[1,2] Pereira C,[1,2] Ivanov M,[4] Soković M,[4] Steinmacher NC,[3] Dias MI,[1,2,*] Barros L.[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[3] Departamento Acadêmico de Alimentos (DAALM), Universidade Tecnológica Federal do Paraná, Campus Medianeira, 85884-000 Paraná, Brasil;
[4] Department of Plant Physiology, Institute for Biological Research "Siniša Stanković", University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia.
*maria.ines@ipb.pt

Las plantas alimenticias no convencionales se presentan como una alternativa viable y eficiente para reemplazar los productos alimenticios que consumimos hoy. Presentando un enorme potencial nutricional, químico, físico y biológico, estas plantas suelen ser abundantes y no competidoras de otras matrices vegetales [1]. *Attalea speciosa* (Mart. Ex Spreng - Babassu) es una palmera que se encuentra en Brasil, y su mesocarpio (MB) representa cerca del 20,4% del fruto, presentando aplicabilidad en la fabricación de alimentos para animales [2]. Así, el presente trabajo tuvo como objetivo profundizar el estudio de la caracterización nutricional de MB por métodos de la AOAC; la determinación del contenido de azúcares libres (HPLC-RI), ácidos grasos (GC-FID), ácidos orgánicos (UPLC-DAD) y compuestos fenólicos (HPLC-DAD/ESI(MS); y propiedades bioactivas (antioxidante, antimicrobiana, antiinflamatoria, citotóxica y nefrotoxicidad) de los extractos hidroetanólicos. Además, se desarrollaron productos de panadería (pan) con 12, 18 y 24% de sustitución de harina de trigo por harina MB. La harina presentó bajos niveles de humedad, grasa y cenizas, siendo los carbohidratos los principales macronutrientes, y los ácidos palmítico y esteárico los principales ácidos grasos. Se identificó tentativamente nueve compuestos fenólicos, seis flavan-3-oles (99% de la cantidad total, sobre todo por la presencia del dímero de (epi)catequina tipo β) y tres flavonoides *O*-glicosilados. El extracto hidroetanólico mostró una alta capacidad antioxidante y antihemolítica, mostrando una IC_{50} de 99% y 75% más efectiva que el control positivo (Trolox), respectivamente. Además, fue capaz de inhibir todas las líneas celulares tumorales, per mostró cierta toxicidad hacia las células sanas. Para la actividad antibacteriana fueron obtenidas concentraciones mínimas inhibitorias inferiores a la de los controles positivos (E211 y E224). Finalmente, se observó que las formulaciones de pan con sustituciones presentaron un aumento razonable en el contenido de PUFAs, manteniendo la capacidad antioxidante con valores de IC_{50} más bajos que los del control positivo, y no presentando actividad hepatotóxica (primera validación de esta harina para la incorporación en matrices alimentarias). En general, la formulación B24 fue la que presentó mayor similitud con el pan control, en relación a los aspectos nutricionales, sin embargo, en cuanto a los parámetros físicos fue la que presentó mayor discrepancia (en volumen específico, textura, y luminosidad). Todas las formulaciones presentaron mayores porcentajes de pérdida de características reológicas en los primeros tres días de elaboración. Este estudio presentó resultados innovadores en cuanto a la caracterización nutricional, química y bioactiva tanto del propio mesocarpio de babasú como del pan elaborado a partir de él, mostrando un gran potencial para ser aplicado en la industria alimentaria, sin embargo, aún queda mucho por explorar, especialmente en preparaciones que todavía no use ingredientes no convencionales.

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Risk assessment of nine coccidiostats in commercial and home raised poultry

André M. P. T. Pereira[1,*], Liliana J.G. Silva[1], Rui R. Martins[1,2], Sofia C. Duarte[1,3],Angelina Pena[1]

[1]LAQV, REQUIMTE, Laboratory of Bromatology and Pharmacognosy, Faculty of Pharmacy, University of Coimbra, Polo III, Azinhaga de Sta Comba, 3000-548 Coimbra, Portugal
[2]Animal Research Centre (CECAV), University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
[3]Centro de Investigação Vasco da Gama, Escola Universitária Vasco da Gama (EUVG), Av. José R. Sousa Fernandes 197, Campus Universitário de Lordemão, 3020-210 Coimbra, Portugal
andrepereira@ff.uc.pt

While total meat consumption is stagnant or decreasing, the amount of poultry meat consumed continues to rise [1]. However, environmental warm and humid conditions, overcrowding, poor hygiene practices, and difficulty to separate infected animals from healthy ones makes poultry very susceptible to coccidiosis [2]. This promotes the widespread use of different coccidiostats in poultry farming and, adding to the resistance to anticoccidials reported globally [3], it poses a risk to consumer's health since they can be found in edible tissues [4]. Therefore, this study aimed to highlight the current situation concerning the different types of poultry production, providing data on 9 coccidiostats in poultry meat samples collected in Portugal. Additionally, this study also aimed to assess the estimated daily intake (EDI) and risk for different population groups, namely, children, adolescents and adults.

To achieve this goal an analytical methodology using solid−liquid extraction followed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) was successfully validated in poultry meat, with limits of detection between 0.9 and 7.4 µg kg^{-1}. This methodology was applied to a total of 101 chicken and turkey samples obtained from canteens, supermarkets, and home productions in Portugal. Halofuginone, diclazuril, decoquinate, narasin, lasalocid, and salinomycin were detected in 20.8% of the samples. The synthetic coccidiostats halofuginone, diclazuril, and decoquinate were found in averages of 0.7 µg kg^{-1}, 2.9 µg kg^{-1}, and 3.7 µg kg^{-1}, respectively, while averages of 1.2 µg kg^{-1}, 1.6 µg kg^{-1}, and 1.3 µg kg^{-1} were found regarding the ionophores narasin, lasalocid, and salinomycin. Home raised samples showed a higher frequency (47.1%). Despite the fact that most of the feeds contain coccidiostats, the reason for these results may be the probable disregard of the withdrawal period, established by European legislation, mainly by domestic breeders, resulting in residues in food matrixes.

As for the risk assessment, values lower than 8.06% (halofuginone) of the acceptable daily intake (ADI) were observed for children using average concentrations. Nonetheless, when considering the worst scenario, these values were up to 53.4% (halofuginone), indicating that exposure to coccidiostats through the consumption of poultry meat does not represent a risk to consumers.

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Efeito de bioestimulantes vegetais nos perfis nutricionais e químicos de *Corylus avellana* L. (avelã)

Liege Aguiar Pascoalino[1,2*], João C.M. Barreira[1,2], M. Ângelo Rodrigues[3], Carlos M. Correia[3], Isabel C.F.R. Ferreira[1,2], Lillian Barros[1,2*], Filipa S. Reis[1,2],

[1]Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[3]Centro de Investigação e Tecnologias Agroambientais e Biológicas (CITAB), Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal.
**liegeaguiar@ipb.pt* *jbarreira@ipb.pt*

O interesse pelas características funcionais dos frutos secos aumentou devido ao seu alto teor em constituintes bioativos. A avelã (*Corylus avellana* L.) é a espécie cultivada mais importante do género *Corylus* (Betulaceae) e é amplamente distribuída pelo mundo [1]. A inclusão destes frutos na alimentação pode ser benéfica devido ao alto percentual de ácidos gordos monoinsaturados e poliinsaturados, tocoferóis e fitoesteróis [2,3]. Com a necessidade do aumento da produção, surge também a necessidade de implementação de uma agricultura mais sustentável. Desta forma, a utilização de bioestimulantes vegetais, em alternativa aos fertilizantes químicos, tem vindo a ser estudada. Neste trabalho, diferentes tipos de bioestimulantes compatíveis com a agricultura orgânica (NPK, Fitoalgas Green® e Sprint Plus®) foram testados em avelãs. Em seguida, foram analisados os parâmetros nutricionais, perfis de ácidos gordos e conteúdo de tocoferóis. A avaliação nutricional das avelãs mostrou que a gordura é o componente maioritário (55% em peso fresco (pf)), sendo o maior teor detetado na linha sem bioestimulantes. Os níveis de proteína foram elevados (16,8g/100g pf), principalmente nas avelãs tratadas com NPK (12% acima do controlo), mas todos os bioestimulantes (exceto fitoalgas) induziram um efeito positivo neste macronutriente. Cinzas e água, componentes minoritários, apresentaram variações mínimas. O valor energético máximo (675 kcal/100 g pf) foi obtido na linha controlo. Em relação aos açúcares solúveis, apenas a sacarose foi identificada com valor médio de 16g/100g pf. O ácido oleico (C18:1n9c) foi predominante, e uma diminuição notável foi observada na avelã, independentemente do bioestimulante, em comparação com o controlo (76%). O ácido linoléico (C18:2n6c), apresentou aumento significativo nas avelãs cultivadas em solos tratados com bioestimulantes, atingindo o valor máximo com o uso de NPK (15,1%). Os níveis de ácido palmítico atingiram maiores percentagens com Sprint Plus® (9,6%), assim como o ácido esteárico (C18:0). De referir que foram encontrados outros ácidos gordos em percentagens vestigiais (soma total inferior a 2%). A concentração de tocoferóis obteve valores médios de 25 mg/100 g pf. Os efeitos mais notórios foram obtidos com as fitoalgas+NPK. Em geral, os bioestimulantes testados induziram aumento nos níveis do ácido linoléico (sobretudo com NPK) e nos níveis de tocoferóis. A importância destes resultados está na possibilidade de selecionar o melhor bioestimulante a ser aplicado e, dessa forma, obter um aumento na quantidade de um composto bioativo específico, possibilitando uma potencial aplicação em alimentos funcionais.

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Efeito de bioestimulantes vegetais nos perfis nutricionais e químicos de amêndoa [*Prunus dulcis* (Miller) D. A. Webb]

Liege Aguiar Pascoalino[1,2,*], Filipa S. Reis[1,2*], M. Ângelo Rodrigues[3], Carlos M. Correia[3], Isabel C.F.R. Ferreira[1,2], Lillian Barros[1,2], João C.M. Barreira[1,2]

[1]Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;

[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;

[3]Centro de Investigação e Tecnologias Agroambientais e Biológicas (CITAB), Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal.

**liegeaguiar@ipb.pt* *freis@ipb.pt*

Os frutos secos são um exemplo de alimentos naturais com efeitos funcionais. A amêndoa [*Prunus dulcis* (Miller) D.A. Webb] é um dos frutos secos mais populares do mundo, ocupando o primeiro lugar nos níveis de produção [1]. No entanto, os elevados níveis de produção geram uma preocupação com uma agricultura menos nociva para o meio ambiente [2]. Assim surgem os bioestimulantes vegetais como alternativa de base biológica projetada para melhorar o desenvolvimento do cultivo e o seu impacto, podem ser usados para substituir ou reduzir a utilização dos fertilizantes químicos convencionais. No presente estudo, diferentes bioestimulantes compatíveis com a agricultura orgânica (Fitoalgas Green®, um extrato de algas marinha de *Ascophyllum nodosum*, Sprint Plus®, um spray foliar rico em aminoácidos, e Tradebor®, um fertilizante de boro para aplicação no solo e foliar) foram testados em pomares de amendoeiras do nordeste de Portugal. Após os tratamentos de campo e colheita, as amêndoas foram analisadas quanto ao valor nutricional, perfil em ácidos gordos e teor de tocoferóis. O perfil nutricional mostrou que a amêndoa é composta principalmente por gordura (55% do seu peso fresco (pf)), com valores máximos na linha não tratada. Nas proteínas, foram obtidos valores próximos a 15g/100g pf. Quanto aos componentes minoritários, cinzas e água, foram observadas variações mínimas, cada uma representando 3g/100g pf. No que diz respeito à energia, o valor máximo (669 kcal/100 g pf) foi obtido na linha controlo. A sacarose foi o único açúcar solúvel identificado, com um teor médio de 12g/100g pf. Os tratamentos com Tradebor induziram um maior teor de sacarose (13g/100g pf). Em relação aos ácidos gordos, o ácido oleico (C18:1n9c) foi o predominante (cerca de 70%), e o seu conteúdo permaneceu quase inalterado apesar do uso de diferentes bioestimulantes, assim como o ácido linoléico (C18:2n6c) (em torno de 16%). Foram também identificados o ácido palmítico (C16:0), ácido esteárico (C18:0), além de outros ácidos gordos em percentagens vestigiais (soma total inferior a 2%). Como na maioria dos alimentos com alto teor de gordura, a concentração de tocoferóis foi elevada (50 mg/100 g pf). Considerando o teor em tocoferóis totais, Fitoalgas Green® induziu um aumento de cerca de 10% (50 a 55 mg/100g pf), nos teores de α-tocoferol e γ-tocoferol. No entanto, todos os outros bioestimulantes testados tiveram o efeito oposto. Os efeitos mais notórios foram obtidos com Fitoalgas Green®, refletido principalmente no aumento do conteúdo de tocoferóis. Devido aos altos níveis de α-tocoferol nas amêndoas, o consumo desses produtos pode aumentar significativamente os níveis de vitamina E na dieta. Assim, a seleção de um melhor bioestimulante pode aumentar a expressão de um composto bioativo específico, agregando maior valor comercial a esses produtos.

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Composição química e bioatividades do epicarpo de *Nephelium lappaceum* L.

<u>Bianca R. Albuquerque</u>[1,2,3*], Maria Inês Dias[1,2], Carla Pereira[1,2], M. Beatriz P. P. Oliveira[3], Isabel C.F.R. Ferreira[1,2], Lillian Barros[1,2,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3] REQUIMTE—Science Chemical Department, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal

**lillian@ipb.pt*

Nephelium lappaceum L., popularmente conhecido como rambutan, é um fruto tropical nativo da Ásia que, atualmente, se encontra amplamente distribuído em outras regiões tropicais, como a América Latina, a Austrália e alguns países africanos [1,2], sendo muito apreciado pela sua aparência exótica e sabor agradável, o que tem aumentado a sua comercialização e processamento em todo o mundo [1-3]. No entanto, apenas uma pequena porção deste fruto é comestível/processado, sendo que até 48% do seu peso corresponde ao seu epicarpo não comestível, o que pode gerar um alto volume de bio-resíduos e perdas económicas [2,3]. No sentido de propor uma valorização para o epicarpo de rambutan como fonte de moléculas bioativas, o presente estudo teve como objetivo elucidar a sua composição química em termos de tocoferóis (HPLC-FD), ácidos orgânicos (UFLC-PDA) e compostos fenólicos antociânicos e não antociânicos (HPLC-DAD/ESI-MSn) e determinar as bioatividades, nomeadamente atividade antioxidante (AA) e atividade antimicrobiana (AM), do seu extrato hidroetanólico por ensaios *in vitro*. A AA foi avaliada através do ensaios de substâncias reativas ao ácido tiobarbitúrico (TBARS) e de inibição da hemólise oxidativa (OxHLIA); a AM foi avaliada pelo método de microdiluição usando seis bactérias (*Staphylococcus aureus, Bacillus cereus, Listeria monocytogenes, Escherichia coli, Salmonella Typhimurium* e *Enterobacter cloacae*) e seis fungos (*Aspergillus fumigatus*, *Aspergillus versicolor*, *Aspergillus niger*, *Penicillium funiculosum*, *Penicillium verrucosum* var. *cyclopium* e *Trichoderma víride).*

O epicarpo de rambutan apresentou três isómeros de tocoferol, sendo o γ-tocoferol o mais representativo; cinco ácidos orgânicos, com destaque para a concentração de ácido chiquímico; cinco compostos fenólicos derivados de elagitaninos e duas antocianinas *O*-glicosiladas derivadas de delfinidina. Em relação às bioatividades, o seu extrato hidroetanólico foi capaz de inibir a oxidação lipídica e proteger os eritrócitos da hemólise oxidativa em baixas concentrações (EC_{50} de 2,79 ± 0,03 e 72 ± 2 µg/mL). Além disso, as atividades antibacteriana e antifúngica do extrato foram alcançadas em concentrações semelhantes ou inferiores aos controlos utilizados (benzoato de sódio (E211) e metabissulfito de potássio (E224)) e as amostras também apresentaram atividade bactericida e fungicida em todos os microrganismos avaliados.

Em conclusão, o epicarpo de *N. lappaceum* possui uma composição química rica em compostos bioativos, principalmente derivados de elagitaninos, além de apresentar boa atividade antioxidante e potencial para inibir o crescimento de microrganismos. Os resultados encontrados revelam que este subproduto pode ser uma interessante fonte de ingredientes bioativos que podem ser aplicados em diversos setores da indústria alimentar e farmacêutica.

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Dietary polyglycosylated anthocyanins, the smart option? Towards their stability and bioavailability

Hélder Oliveira[1], Catarina Roma-Rodrigues[2], Iva Fernandes[1], Alexandra Fernandes[2], Pedro Baptista[2], Victor de Freitas[1], Nuno Mateus[1]

[1]REQUIMTE/LAQV, Chemistry and Biochemistry Department, Faculty of Sciences, University of Porto, Portugal
[2]REQUIMTE/UCIBIO, Departamento de Ciências da Vida, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa
helder.oliveira@fc.up.pt

Over the years, anthocyanins have emerged as one of the most enthralling groups of natural phenolic compounds. The interest raised around anthocyanins goes way beyond their visually appealing colors and their acknowledged structural and biological properties have fueled intensive research towards their application in different contexts. However, the high susceptibility of monoglycosylated anthocyanins (MGA) to degradation under certain external conditions might compromise their applications and health properties. In that regard, polyglycosylated anthocyanins (PGA) might offer an alternative to overcome this issue, owing to their peculiar structure and consequent less predisposition to degradation [1].

PGA from different food sources (purple sweet potato, red wine, *Cosmos bipinnatus, Centaurea cyanus* and *Viola tricolor* edible flowers) were isolated and structurally characterized. The stability at different pH was evaluated by means of pH jumps. Thermal stability was also evaluated. Furthermore, their stability to the digestion processes was performed in vitro at the oral, gastric and intestinal level. Transepithelial transport assays were performed using gastric and intestinal celular models to evaluate the absorption and role of food matrices. Also, a nano-gene-silencing technology with gold nanoparticles allowed the evaluation of the molecular mechanism of absorption of these anthocyanins. Laser Scanning Confocal Microscopy was used to track PGA in gastric and intestinal cells.

The results suggested a higher stability at a broader range of pH values (with lower hydration and higher acidity constants) when compared to the already published kinetic and equilibrium parameters of MGA, and a higher thermal stability up to 100 celsium degrees and pH 7 (with more than 50% of total PGA detected when compared to MGA).

The digestions studies revealed a higher resistance of acylated PGA at the different levels (with significant differences up to 30% when compared with MGA) and the transport studies revealed a structure-absorption efficiency relation at both gastric and intestinal level in the presence and absence of food matrix, with the more complex structures presenting a lower transport efficiency. Also, specific food matrix components such as proteins and glucose had a tremendous negative effect on the transport efficiency of the anthocyanins.

Furthermore, the involvement of Glucose Transporters 1 and 3 (GLUT1 and GLUT3) on the transport mechanism of PGA was observed, through a significant reduction of the transport efficiency of the anthocyanins up to 50% upon the silencing of the transporters. And upon incubation, PGA seems to be concentrated in specific cell areas, suggesting localized bioactive actions.

These results elucidate new insights on PGA stability and bioavailability and suggest that this subclass on anthocyanins may be more appealing for both nutritional, health and technological applications.

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Comparação do efeito de diferentes poliaspartatos de potássio na estabilização tartárica e na filtrabilidade do vinho

J. Carvalho[1], H. Mira[1,2]*

[1] Escola Superior Agrária - Instituto Politécnico de Santarém, Quinta do Galinheiro, 2001-904 Santarém, Portugal

[2] CIEQV - Centro de Investigação em Qualidade de Vida, Instituto Politécnico de Santarém e Instituto Politécnico de Leiria. Avenida Dr. Mário Soares N.º 110. 2040-413 Rio Maior, Portugal. (FCT, projetos UIDB/04748/2020; UIDP/04748/2020)

**helena.mira@esa.ipsantarem.pt*

A precipitação dos cristais dos sais do ácido tartárico, nomeadamente o hidrogenotartataro de potássio é um problema de instabilidade físico-química de ocorrência muito comum nos vinhos.

Há uma nova geração de produtos enológicos para a promoção da estabilidade tartárica, produtos à base de poliaspartato de potássio [1, 2]. O objetivo deste trabalho foi comparar o efeito de quatro produtos à base de poliaspartato de potássio (*Antartika V40, Antartika VR, Antartica Fresh* e *Antartica Duo*) na estabilidade tartárica, na turbidez e na filtrabilidade dos vinhos, nomeadamente no Índice de colmatagem (IC) e volume máximo de filtrado (Vmax.). Foram aplicadas duas doses de cada produto (d_1=dose mínima e d_2=dose máxima, recomendadas) a vinho branco, vinho rosado e vinho tinto. Avaliou-se também o efeito destes produtos ao longo do tempo: aos 7 dias, um mês, três meses e cinco meses.

Os quatro produtos revelaram promover a estabilidade tartárica dos três tipos de vinho para as duas doses aplicadas e ao longo do tempo de estudo, exceto o *Antartica Duo* para o vinho branco. O vinho branco com *Antartica Duo* apenas apresentou estabilidade tartárica no tempo 1 (sete dias após a aplicação), confirmando que este produto não é recomendado para vinho branco.

A análise estatística dos dados foi realizada com o *Statistical Package for the Social Sciences* (SPSS) 27 para Windows (SPSS, Inc., Chicago, IL, USA), tendo-se utilizado o teste não paramétrico de Kruskal-Wallis. Nos resultados obtidos para o vinho branco, não se verificaram diferenças significativas ($p<0.05$) relativamente à turbidez, ao índice de colmatagem e ao volume máximo filtrado, entre os *produtos Antartika V40* e *Antartika Fresh,* e entre *Antartika VR e Antartica Duo*. Verificaram-se diferenças significaticas entre o vinho controlo (sem aplicação de poliaspartato) e a dose 2 para os parâmetros turbidez, IC e Vmax, tendo-se ainda verificado diferenças entre a dose 1 e a dose 2, relativamente à turbidez e Vmax.

No vinho rosado, não se observaram diferenças significativas entre os diferentes produtos aplicados para o IC e o Vmax. O vinho em que foi aplicado o *Antartika V40* apresentou turbidez significativamente menor, que a dos vinhos com aplicação dos outros produtos em estudo. Quanto à dose aplicada, verificaram-se diferenças significativas entre o vinho controlo e a dose 2 para os parâmetros analisados.

No vinho tinto, verificaram-se diferenças entre os produtos aplicados no que se refere ao IC, ao Vmax e à turbidez, assim como entre a dose 2 e o vinho controlo; registaram-se ainda, diferenças significativas ao longo do tempo para os parâmetros em estudo.

O poliaspartato de potássio revelou-se eficaz na promoção da estabilidade tartárica, sem contribuir para o aumento da turbidez dos vinhos, nem afetar a filtrabilidade dos mesmos.

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Multielement analysis as a discriminating tool of PDO and PGI food products

Ana M.S. Costa[1,*], Elisabete Coelho[1], Lina Carvalho[2], Eugénio Soares[2], Eduarda Pereira[1,2], Manuel A. Coimbra[1]

[1] Chemistry Department, LAQV – REQUIMTE, University of Aveiro, Campus Universitário de Santiago, Aveiro 3810-193, Portugal.

[2] Central Laboratory of Analysis (LCA), University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal.

**anamariacosta@ua.pt*

The food product label as Protected Designation of Origin (PDO) or Protected Geographical Indication (PGI) is a guaranty of authenticity and traceability. PDO “Pera Rocha do Oeste” pear, PDO “Queijo da Serra da Estrela” (SE) cheese, PDO “Azeitão” cheese and PGI “Maçã de Alcobaça” apple, due to its *sui generis* characteristics, are important Portuguese products due to its economic value to Portugal. Apple and pear fruits have their consumption in fresh, as well as industrially processed. It is possible that the fruits of a region possess characteristics associated to the environment [1], conferring them these required unique characteristics for their identification, even when processed. In case of PDO cheeses, they are cured cheeses, obtained by slow depletion of the curd after coagulation of raw sheep's milk by the action of the cardoon (*Cynara cardunculus*, L.) enzymes [2,3]. It is very important economically to be able to distinguish the different PDO cheeses, once both PDO “Queijo da SE” cheese and PDO Azeitão cheese are made from sheep's milk.

In this study, the element profiles, analysed by Inductively Coupled Plasma (ICP), of PDO products (“Pera Rocha do Oeste”, “Queijo da SE and Azeitão cheese) and PGI products ("Maçã de Alcobaça”) were identified to evaluate the applicability of multielement data on the determination of geographical origin and authenticity. PDO pears are discriminate from non PDO ones by 13 elements. The PDO industrial processed pears are also discriminated from the non PDO by 4 elements (Mn, Ce, B and Rb). For PDO cheeses, the element Cs, Ba, Rb, Mn, Zn, Fe, Sr and Cu discriminate SE cheeses from Azeitão products. Multielement analysis was also able to distinguish PGI fresh and processed apples with Cs and Rb concentrations present in lower amounts. These elements were related with orchards and pasture soil origin.

The present study shows that multielement analysis combined with the statistical tools can be a valuable contribution for the identification and authenticity of the geographical origin of PDO and PGI food products.

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Adansonia digitata L. (mukua): um possível alimento funcional

Filipa A. Fernandes[1,2,3], **Márcio Carocho**[1,2], **Ricardo C. Calhelha**[1,2], **Tânia C.S.P. Pires**[1,2], **José Carlos Freitas**[4], **Miguel A. Prieto**[3], **Sandrina A. Heleno**[1,2*], **Lillian Barros**[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3]Grupo de Nutrición y Bromatología, Departamento de Química Analítica y Alimentaria, Facultad de Ciencias de Ourense, Universidad de Vigo-Ourense Campus, E-32004 Ourense, Spain

[4]Goldenpuzzle Lda. Rua Santos Pousada Nr.441 4000-487 Porto, Portugal

**sheleno@ipb.pt*

Adansonia digitata L. é espécie africana com vários usos tradicionais, nomeadamente medicinal e alimentar [1,2]. A polpa do seu fruto, comumente conhecido como mukua, está aprovada como um ingrediente alimentar pela Comissão Europeia e pela “Food and Drug Administration of the United States of America” [1]. Assim o objetivo deste trabalho foi comprovar a potencialidade da polpa da mukua como um alimento funcional através da sua caracterização nutricional, mineral e bioativa. O perfil nutricional foi obtido aplicando metodologias oficiais de análise AOAC [3]. O conteúdo mineral foi determinado por espectrofotometria de absorção atómica e o potencial bioativo foi determinado através da atividade antioxidante pelo ensaio antioxidante celular (CAA) e um ensaio de inibição de substâncias reativas do ácido tiobarbitúrico (TBARS). Além disso, a atividade antimicrobiana foi também determinada, através do método de microdiluição, e a atividade antitumoral foi avaliada em três linhas celulares tumorais humanas: adenocarcinoma gástrico (AGS), carcinoma de mama (MCF-7), células de carcinoma de pulmão (NCI-H460), e a citotoxicidade em culturas de células não tumorais de rim de macaco africano (VERO), através do ensaio da Sulforrodamina B.

Relativamente aos resultados obtidos, a polpa de mukua apresentou um teor de humidade muito baixo (11,9 + 0,3 g/100 g ms). Os macronutrientes presentes em maior quantidade foram os hidratos de carbono (89,6 ± 0,2 g/100 g ms), seguidos das proteínas (2,7 ± 0,3 g/100 g ms) e da gordura bruta (1,8 + 0,1 g/100 g ms), representando um valor energético de 386 ± 1 kcal/100 g ms. Quanto ao perfil mineral, a amostra revelou um alto teor em potássio (20,4 ± 0,8 g/100 g ms), estando também presentes minerais como o magnésio (3,28 ± 0,08 g/100 g ms), o cálcio (2,79 ± 0,07 g/100 g ms), o manganês (2,02 ± 0,09 g/100 g ms) e o ferro (1,53 ± 0,09 g/100 g ms). Em relação à atividade antioxidante, a polpa inibiu cerca de 32% da oxidação celular no método CAA e exibiu um valor de EC_{50} de 23,0 ± 0,1 μg/mL no ensaio de TBARS. Para a atividade antimicrobiana, a polpa apresentou atividade bacteriostática contra a maioria das bactérias testadas. No ensaio de citotoxicidade, a polpa demonstra capacidade de inibir a proliferação celular contra as linhas tumorais testadas, principalmente contra AGS com valores de GI_{50} de 92 ± 1 μg/mL, sem toxicidade para as células não-tumorais.

Este estudo mostra que a polpa de mukua, além de ser nutricionalmente interessante, possui alto teor em minerais, nomeadamente em potássio que é um composto essencial para a bom funcionamento do corpo, estando associado à prevenção de doenças como diabetes, osteoporose e ainda doenças cardiovasculares. Além disso, a polpa da mukua possui alto potencial bioativo, o que indica que o seu consumo pode oferecer benefícios para a saúde, tornando-o num potencial alimento funcional.

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ALM16

HAEMATOCOCCUS PLUVIALIS COMO ADITIVO EN LA COLORACIÓN Y MEJORA DE LAS PROPIEDADES ORGANOLÉPTICAS Y NUTRICIONALES DE ALIMENTOS

Aly Castillo[1,2], Tiane C. Finimundy[3], Sandrina A. Heleno[3], Paula Rodrigues[3], Filipa A. Fernandes[3], Carmen Garcia-Jares[1,2], Lillian Barros[3], Marta Lores[2]

[1]CRETUS, Departamento de Química analítica, Nutrición y Bromatología, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España
[2]LIDSA, Departamento de Química analítica, Nutrición y Bromatología, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España
[3]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, Bragança, 5300-253, Portugal.
alyjesus.castillo.zamora@usc.es

En la industria alimentaria preocupa el amplio uso de colorantes artificiales derivados principalmente del sector petroquímico [1]. Por otra parte, además de no aportar ningún valor añadido más allá de la coloración, estos tintes pueden presentar efectos adversos para la salud [2]. En respuesta a estos problemas globales, este trabajo aporta una alternativa natural a los aditivos artificiales, mediante la aplicación de la pasta húmeda de la microalga *Haematococcus pluvialis* (HPW) en fase roja, rica en astaxantina, como sustituto parcial de la harina de trigo (7% y 13% p/p) en la elaboración de filloas, un postre típico del noroeste de la Península Ibérica, que combina los ingredientes básicos de la repostería industrial. El perfil nutricional de las muestras enriquecidas con la pasta de microalgas se evaluó mediante un análisis comparativo con un colorante alimentario sintético (Fig. 1). Se obtuvo un contenido total de carotenoides (843 µg/g) y ácidos grasos (76 mg/g) para la filloa con el máximo nivel de adición de *H. pluvialis* en contraste con una respuesta no significativa del colorante artificial. Posteriormente, se evaluó la estabilidad del color de la filloa fortificada a lo largo del tiempo (3, 6 y 9 días) así como sus propiedades fisicoquímicas y su perfil microbiológico para determinar la funcionalidad de la pasta de alga húmeda como conservante alimentario. Como resultado, HPW proporcionó una filloa de color rojo natural con una mayor vida útil y brillo (*L) en relación con una mezcla de colorante rojo sintético. La textura de las filloas que contenían *H. pluvialis* mostró una conservación significativa ($p<0,02$) durante los primeros 6 días, mejorando la dureza y la extensibilidad en relación con el control. El enriquecimiento de carotenoides y ácidos grasos, en combinación con un potencial moderador de la degradación microbiológica por parte de este organismo unicelular, da un valor añadido a esta matriz alimentaria.

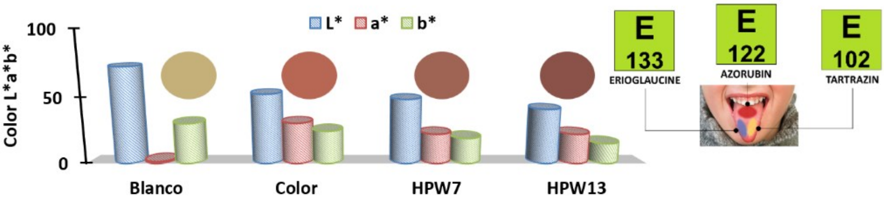

Fig.1. Análisis comparativo del perfil de color (L*a*b*) de las filloas. Blanco: grupo control; Color: adición colorante sintético; HPW7 y HPW13: adición de *H. pluvialis* al 7% y 13% ($g·100g^{-1}$) respectivamente.

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Flavylium-based host-guest systems for biogenic amine sensing during food spoilage

Ana Sofia Pires,[1] Nuno Basilio,[2] Vânia Gomes,[1] Nuno Mateus,[1] Victor de Freitas,[1] Luís Cruz[1,*]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Porto, Portugal.
[2]Laboratório Associado para a Química Verde (LAQV), REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal.
Corresponding author: luis.cruz@fc.up.pt; Tel.: +351 220402558; fax: +351 220402658

Food quality and safety is a central issue in today's food economics mainly due to the growing demands of consumers. Biogenic amines are biologically active nitrogen-containing compounds that are undesirable in food and can cause significant health problems [2]. The main goal of this work was the development of colorimetric/fluorescent host-guest molecular switches based on interactions between a bioinspired 10-methylpyrano-4'-hydroxyflavylium [3] guest dye and sulfonated-based macrocycle hosts (calix[n]arenes and captisol) with sensing ability for biogenic amines, evaluated through UV-Vis and fluorescence spectroscopy.

The macrocycle-dye systems were optimized in terms of molecular ratio and the working pH considering de pK_a value of free pigment (pK_a 6.72) and the complexes (e.g., pK_a 8.45). Overall, in a phosphate buffer solution (pH 7.2-7.6), the complexes were able to encapsulate putrescine/tyramine in solution with concomitant release of the quinoidal base species of dye to the bulk, with colorimetric variation from yellow to pink-red. The biogenic amines sensing were also detect by distinct fluorescent events showing a host structural-dependency: a fluorescence enhancement for the dye: calix[n]arene complexes and a fluorescence quenching for the dye: captisol complex. This host-guest system demonstrated great potential for the detection of biogenic amines, one of the main key markers of food spoilage.

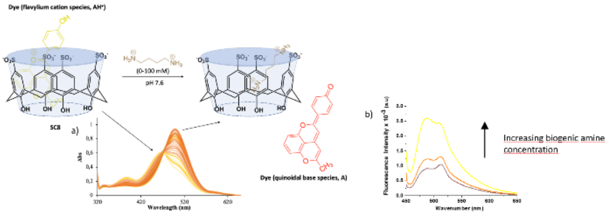

Fig 1: Example of the Dye-SC8 (0.05:0.5 mM) system in the presence of increasing concentrations of putrescine (0-100 mM) at pH 7.6 monitoring by a) UV-Vis spectroscopy and b) fluorescence spectroscopy

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Effects of gastrointestinal digestion on the bioactive properties and phlorotannin profile from *Laminaria digitata*

Marcelo D. Catarino[1,*], Rocio Villalba[2], Bruno Neves[3], Débora Campos[4], Artur M. S. Silva[1], Manuela Pintado[4], Francisco Tomás-Barberán[2], Susana M. Cardoso[1]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Laboratory of Food and Health, CEBAS-CSIC, Food Sci. & Technology Deptartment, E-30100 Murcia, Spain
[3] Department of Medical Sciences and Institute of Biomedicine—iBiMED, University of Aveiro, 3810-193 Aveiro, Portugal
[4] CBQF—Centro de Biotecnologia e Química Fina—Laboratório Associado, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, 4169-005 Porto, Portugal
**mcatarino@ua.pt*

Phlorotannins are phenolic compounds made of several units of phloroglucinol that are exclusive from brown macroalgae and have been recognized for their promising bioactive properties [1]. However, the bioactive properties described for these compounds have usually been described on pure compounds and/or phlorotannin-rich extracts without considering the possible alterations that they may incur during their passage of the gastrointestinal tract. In this study, a phlorotannin extract was obtained from *Laminaria digitata*, an edible brown seaweed species that grows profusely along the shores of the north-east Atlantic. After being submitted to a simulated gastrointestinal digestion following the infogest protocol, a reduction of their concentration and consequent loss of antioxidant activity measured in vitro via $NO^{\bullet}$ and $O_2^{\bullet-}$ scavenging assays, thus suggesting that these compounds' integrity and bioactivity are negatively affected by the digestive process. Indeed, data collected from UHPLC-ESI-MS/MS analysis revealed interesting differences between the phlorotannin profiles of non-digested versus digested extracts, especially when looking at the fuhalol-type compounds, since these were completely absent in the digested extract. Nevertheless, when non-digested vs digested extracts were used on LPS-stimulated Raw 264.7 macrophages, both showed strong inhibitory effect on the cellular $NO^{\bullet}$ production, suggesting that even though there is a decrease of the phlorotannins' concentration after digestion with consequent loss their scavenging properties, the possible products that are being formed either by degradation or by interation with other components of the digestive médium, may exert their effects through the modulation of the intracellular signaling mechanisms.

Overall, this study not only contributed to a better understanding of the impact of gastrointestinal digestion in the phlorotannin profile of *L. digitata* extract, but also allowed to understand that, although the digestive process may affect total content of phlorotannins, it does not necessarily translate into loss of bioactivity, in particular the anti-inflammatory activity, most likely owing to the possible bioactive effects that the products formed during the digestion may have on intracellular level.

Acknowledgements:

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Application of data mining techniques to unveil contaminants occurrence in food

<u>Zita E. Martins</u>[1,*], Marta Silva[1], Armindo Melo[1,2],Miguel A. Faria[1], Isabel M.P.L.V.O. Ferreira[1]

[1]LAQV/REQUIMTE, Laboratory of Bromatology and Hydrology, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, 4050-313, Portugal
[2]Instituto Nacional de Saude Dr. Ricardo Jorge, Departamento de Saúde Ambiental, Rua Alexandre Herculano 321, Porto, 4000-055, Portugal
**zmartins@ff.up.pt*

The influence of diet in human health is undeniable and chemical components, such as contaminants, may have a relevant role as factors contributing to several diseases. However, the lack of systematic data on food composition hinders the ability to explore how contaminants in food affect health.

The goal of this work was to carry out a broad systematic review of literature using FoodMine's code [1], with some modifications to mine and collect all available data on 96 contaminants and 7 foods from animal products. This is a process not feasible to carry out manually.

The initial number of papers retrieved by PubMed ranged from 21 (mutton) to 967 (egg). The application of FoodMine machine learning algorithm identified between 7 (goat) to 18 (turkey) % of the papers as useful. After a manual revision of those papers, data were collected from 0 (goat) to 41 (beef) % of them. As shown in Fig. 1, from the 7 foods mined, beef and chicken were the ones with higher number of papers with relevant information. Overall, HAAs, PAHs, and metals were the contaminants groups with higher frequency across the different foods. Moreover, no data was collected regarding dioxins/furans/PCBs and disinfection by-products groups. Regarding quantities of contaminants found (Tabla 1), higher mean values were reported for metals, followed by HAAs and PAHs. Additionally, beef and chicken stood out with higher mean values for these contaminants. No trends could be identified for mycotoxins and pesticides since they were only found for egg.

Besides collecting relevant data, this work also revealed a meaningful pattern of contaminants' prevalence in this food group.

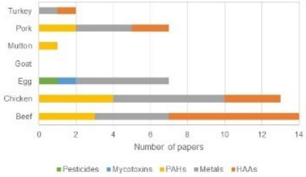

Fig.1. Frequency of papers with information collected for different foods from animal origin

Tabla 1. Values of contaminants (µg/kg) found in different foods from animal origin (mean (min–max))

Food	HAAs	Metals	PAHs	Mycotoxins	Pesticides
Beef	80.09 (0.01–2106.97)	711.79 (4.90–18900.00)	8.66 (0.01–194.14)	na	na
Chicken	3.72 (0.01–27.52)	225.16 (1.42–2228.50)	1.26 (0.01–51.00)	na	na
Egg	na	107.5 (1.00–1061)	na	0.49 (0.01–0.92)	25.67 (0.03–226.00)
Goat	na	na	na	na	na
Mutton	na	na	0.62 (0.62–0.62)	na	na
Pork	2.37 (0.02–10.11)	14.80 (5.10–46.60)	1.73 (0.01–42.73)	na	na
Turkey	1.00 (0.00–2.02)	15.13 (1.18–28.92)	na	na	na

na, not available

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Caracterização química e propriedades bioativas de resíduos industriais da produção de óleo de noz (*Juglans regia* L.)

Rafael Mascoloti Spréa[1,2,3], **Tiane C. Finimundy**[1,2], **José Pinela**[1,2], **Ricardo C. Calhelha**[1,2], **Tânia C.S.P. Pires**[1,2], **Joana S. Amaral**[1,2*], **Miguel A. Prieto**[3], **Lillian Barros**[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal.
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Bragança, Portugal.
[3]Grupo de nutrição e bromatologia, Universidade de Vigo, Ourense, Espanha
**jamaral@ipb.pt*

As borras obtidas na produção de óleo de noz podem ser consideradas como um dos principais subprodutos desta indústria, sendo atualmente reaproveitados como fertilizante ou na alimentação animal [1]. Neste sentido, tendo por objetivo final a valorização deste subproduto, este trabalho consistiu na caracterização química e avaliação da bioatividade das borras geradas na produção de óleo de noz.

As borras industriais foram analisadas no que respeita o teor em açúcares livres e tocoferóis usando cromatografia líquida acoplada a detetores de índice de refração (HPLC-RI) e de fluorescência (HPLC-FL), respetivamente. Os ácidos gordos foram determinados por cromatografia gasosa com deteção de ionização de chama (GC-FID), os ácidos orgânicos por cromatografia líquida ultrarrápida acoplada a um detetor de díodos (UPLC-DAD) e os compostos fenólicos por HPLC com deteção DAD e espectrometria de massa (HPLC-DAD-ESI-MS/MS). Adicionalmente, avaliou-se a atividade antioxidante e antimicrobiana do extrato hidroetanólico obtido a partir das borras. A atividade antioxidante foi determinada através de três ensaios *in vitro* (inibição da peroxidação lipídica por substâncias reativas ao ácido tiobarbitúrico (TBARS) em homogeneizados cerebrais, e atividade antioxidante celular (CAA)) e a atividade antimicrobiana pelo método de microdiluição contra um painel de bactérias e fungos.

As borras de nozes apresentaram uma predominância em ácidos gordos polinsaturados, sendo o ácido linoleico o maioritário, apresentando um teor superior a 55%. Em relação aos tocoferóis, foram observadas as isoformas α, γ e δ, sendo o γ-tocoferol o composto predominante (89 mg/100 g). Apenas a sacarose foi identificada no que concerne os açucares livres, e o ácido quinico foi o maioritário (1,06 mg/100 g) entre os cinco ácidos orgânicos identificados. No que respeita a composição fenólica do extrato, observou-se uma predominância de derivados da catequina (flavan-3-ois) e taninos hidrolisáveis. O extrato das borras de nozes demonstrou interessante atividade antioxidante, apresentando ótimos valores de EC_{50} (TBARS: 32,84 μg/mL) e % de inibição (CAA: 90%). Contudo, o extrato não apresentou atividade significativa contra as bactérias e fungos testados. Os resultados deste trabalho demonstram o potencial deste resíduo industrial dada a sua elevada atividade antioxidante e composição em nutrientes e compostos bioativos, podendo o mesmo ser futuramente explorado através da sua incorporação em produtos alimentares, agregando valor à cadeia produtiva de óleo de noz.

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Avaliação de subprodutos de soja (*Glycine max*), uma potencial fonte de nutrientes e compostos bioativos

Rafael Mascoloti Spréa[1,2,3], Tiane C. Finimundy[1,2], José Pinela[1,2], Ricardo C. Calhelha[1,2], Tânia C.S.P. Pires[1,2], Joana S. Amaral[1,2], Miguel A. Prieto[3], Lillian Barros[1,2*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal.
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Bragança, Portugal.
[3]Grupo de nutrição e bromatologia, Universidade de Vigo, Ourense, Espanha
**lillian@ipb.pt*

A soja (*Glycine max*) tem desempenhado um papel relevante na alimentação humana do século 21, não só através de produtos à base do grão, como pelo seu óleo, mas também pela sua utilização na produção de bebida vegetal [1]. Esta última tem-se tornado cada vez mais popular, aumentando a quantidade de grão de soja utilizado e, consequentemente, a quantidade de resíduos gerados. Por forma a contribuir para a implementação de uma economia circular, este trabalho teve como objetivo a caracterização química e nutricional de subprodutos provenientes da indústria de produção de bebidas vegetais de soja, nomeadamente okara e casca de soja.

A composição proximal dos resíduos foi determinada pelos métodos oficiais da AOAC, os açúcares livres, tocoferóis e ácidos orgânicos por cromatografia líquida com detetor de índice de refração (HPLC-RI), de fluorescência (HPLC-FL) e de díodos (UPLC-DAD), respetivamente, o perfil de ácidos gordos por cromatografia gasosa com detetor de ionização de chama (GC-FID), e os compostos fenólicos por HPLC acoplado a um DAD em série com espectrometria de massa (HPLC-DAD-ESI-MS/MS). Adicionalmente, procedeu-se à avaliação da atividade antimicrobiana face a oito estirpes bacterianas multirresistentes causadoras de doenças alimentares e duas estirpes de fungos contaminantes de alimentos, e da atividade antioxidante pelos ensaios de inibição da peroxidação lipídica (TBARS), inibição de hemólise oxidativa (OxHLIA) e atividade celular antioxidante (CAA).

Relativamente ao okara, este subproduto apresentou elevada humidade, sendo o macronutriente predominante as proteínas. Na casca, verificou-se uma predominância de carboidratos e fibras, e baixo teor de humidade. Na fração lipídica, ambos os subprodutos apresentaram uma predominância de ácidos gordos polinsaturados, sendo os maioritários os ácidos oleico e linoleico para o okara e para a casca, respetivamente. Foram detetadas 3 isoformas de Vitamina E, sendo o γ- e δ-tocoferol identificados no Okara, e o α- e δ-tocoferol na casca do grão de soja, verificando-se uma predominância de δ-tocoferol em ambos os subprodutos. O ácido oxálico foi o único ácido orgânico identificado no okara, enquanto o ácido cítrico foi o predominante na casca de soja. Os elagitaninos e isoflavonas foram os compostos fenólicos maioritários na casca dos grãos de soja, sendo as isoflavonas igualmente predominantes no okara. Ambos os extratos apresentaram propriedades antioxidantes satisfatórias, e no geral apresentaram uma inibição superior contra o crescimento de fungos comparativamente a bactérias. Os resultados obtidos demonstram que os subprodutos de soja têm uma composição interessante do ponto de vista nutricional, podendo ser uma fonte de compostos bioativos e um recurso para o desenvolvimento de novos ingredientes funcionais para a indústria alimentar.

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Sandoricum koetjape fruit juice inhibits 5-lipoxygenase and interferes with the inflammatory response of activated BV-2 cells

Ana C. Moura-de-Carvalho[1,*], Sutsawat Duangsrisai[2], Paula B. Andrade[1], Diana C.G.A. Silva[3], Nelson G. M. Gomes[1]

[1] REQUIMTE/LAQV, Laboratório de Farmacognosia, Departamento de Química, Faculdade de Farmácia, Universidade do Porto, R. Jorge Viterbo Ferreira, nº 228, 4050-313 Porto, Portugal.
[2] Department of Botany, Faculty of Science, Kasetsart University, Ngam Wong Wan Road, Chatuchak, Bangkok 10900, Thailand
[3] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, 3810-193, Portugal
**up201809608@ff.up.pt*

Due to the current gaps in pharmacotherapeutic approaches to target chronic neuroinflammation, phytochemicals with neuroprotective and anti-inflammatory properties are increasingly being screened and proposed as a viable option through their standardized incorporation into plant-derived products [1]. Access to a collection of barely investigated '*superfruits*' from Thai flora enabled to characterize the impact of santol (*Sandoricum koetjape* (Burm.f.) Merr.) against mediators of the neuroinflammatory process. The juice obtained from *S. koetjape* fruit has shown relevant scientific outcomes, causing a significant reduction on NO levels in BV-2 microglial cells (**A**) and in a cell-free system (**B**). Significant effects upon lipid peroxidation were also recorded, namely by targeting 5-lipoxygenase, causing a significant inhibition down to values ranging from 44 to 73% at the full range of concentrations (31.25-1000 µg mL^{-1}) (**C**), as well as through an antiradical effect. UHPLC-DAD-ESI-MS^2 profiling allowed to identify a series of previously unreported caffeic, coumaric and ferulic acid derivatives, most of which occurring as ester conjugates of quinic acid. The cumulative preclinical and clinical data on the anti-inflammatory effects of specific phenolic constituents identified in *S. koetjape* juice, allows to provide the chemical basis on the *in vitro* recorded effects [2]. Overall, our study sets the cornerstone to the development of a novel edible product to hamper the effects of neuroinflammation, based on the richness in specific anti-inflammatory bioactives.

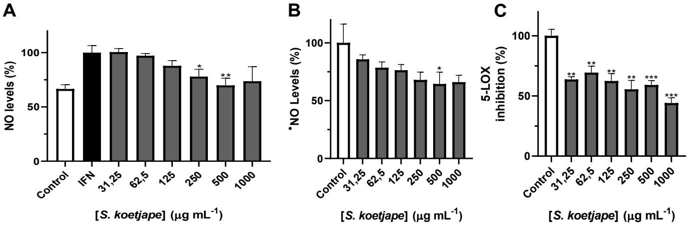

Fig.1. Effects of *S. koetjape* fruit juice on NO levels in cell-based (**A**), in cell-free system (**B**) and on the activity of 5-LOX (**C**). Results correspond to the mean ± SD of three independent experiments performed in triplicate (statistical significance: * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$)

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Combinação de diferentes regimes de fertilização e irrigação para a produção de cardo dourado (*Scolymus hispanicus* L.) de alto valor nutricional e mineral

Paschoalinotto B. H.[1,2,3]; Prieto M.A.[3]; Polyzos N.[4]; Compocholi M.[4]; Petropoulos S.A.[4]; Barros L.[1,2]; Dias M.I.[1,2,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[3] Grupo de Nutrición y Bromatología, Departamento de Química Analítica e dos Alimentos, Facultade de Ciencia e Tecnoloxía dos Alimentos, Universidade de Vigo, Campus de Ourense, 32004 Ourense, España;
[4] Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 38446 Volos, Greece.
**maria.ines@ipb.pt*

Scolymus hispanicus L. (cardo dourado) é uma planta silvestre comestível que foi popularmente inserida no passado na Dieta Mediterrânica e que caiu em desuso em prol de outras espécies mais apreciadas pelo consumidor [1]. Considerando a atual preocupação por uma alimentação mais funcional e, consequentemente, mais saudável dos consumidores, a par da perda de biodiversidade pela colheita irracional de espécies silvestres de alto valor acrescentado, é de extrema importância desenvolver uma produção racional, padronizada e sustentável destas plantas com um perfil nutricional e mineral que se coadunem com as exigências dos consumidores. A otimização dos regimes de fertilização e o uso racional da água têm sido dos fatores mais estudados pela academia e implementados pelos agricultores para aumentar o rendimento das suas culturas [2,3]. O objetivo do presente estudo foi avaliar o efeito da fertilização com soluções nutritivas contendo diferentes proporções de azoto, fósforo e potássio (N:K:P) bem como o efeito do regime de irrigação no perfil nutricional e mineral das folhas de *S. hispanicus*. Os conteúdos de proteína bruta (Pr), gordura (G), cinzas (C) e fibras dietéticas (FD) totais foram avaliados através de métodos AOAC e hidratos de carbono (HC) por diferença. O conteúdo de minerais avaliado por feito por AAS. A energia foi calculada de acordo com a equação: 4 x (g Pr + g HC) + 2 x (g FD) + 9 x (g G). Os controlos usados foram produzidos sem fertilização (SHFC) e com irrigação feita com água da chuva (SHIC).

Os regimes de irrigação tiveram um maior impacto positivo no conteúdo de Pr, C e FD totais quando do que os regimes de fertilização via solução nutritiva, revelando maiores teores desses macronutrientes funcionais e consequentemente, menores teores de HC. O conteúdo de G não foi afetado. A fertilização com 300:200:100 ppm (N:P:K) revelou o maior conteúdo energético bem como de HC. O perfil mineral obtido em todos os tratamentos aplicados foi bastante distinto, o que era expectável. Com a produção em hidroponia acoplada à irrigação foram obtidos maiores teores de ferro, cálcio e potássio; no entanto o controlo em hidroponia apresentou maiores teores de sódio. A maior concentração de manganês foi obtida nas amostras com irrigação de 100:100:100 ppm (N:P:K).

Os impactos dos diferentes regimes de fertilização e irrigação na qualidade nutricional e conteúdo mineral são evidentes; sendo necessários para o desenvolvimento de sistemas agrícolas sustentáveis.

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Quantificação e caracterização do conteúdo de polifenóis em produtos de maçã

Teixeira JC,[1] **Soares S, Pérez R, Mateus N, De Freitas V,**

REQUIMTE, LAQV, Departamento de Quimica e Bioquimica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

[1] *jcmoreira@fc.up.pt*

Os polifenóis resultam do metabolismo secundário das plantas e têm ganho grande atenção devido às suas bioactividades amplamente comprovadas (1,2). Graças à sua actividade antioxidante, os polifenóis podem reverter o stress oxidativo promovido pelos radicais livres, sendo importantes na defesa contra várias patologias como o cancro, infecções microbianas, doenças cardiovasculares, ajuda no controlo dos sintomas da menopausa, e muitas outras(1-3). Entre as fontes ricas em polifenóis destacam-se as maçãs que baixam o nível de colesterol e triglicéridos prevenindo o cancro, aterosclerose, diabetes mellitus, e Alzheimer(2). A maçã, a principal fruta consumida em Portugal, foi descrita com mais de 60 compostos de polifenóis (1). O teor de polifenóis nas maçãs depende da origem geográfica ou variedade. Além disso, as técnicas de processamento aumentam, diminuem ou modificam o seu perfil em compostos de polifenóis(3).

Este estudo visa compreender o efeito do processamento de maçãs no perfil do polifenol para obter sumo dependendo de 1) centrifugação e 2) temperatura. As amostras foram preparadas numa empresa nacional da indústria alimentar com diferentes temperaturas e velocidades de centrifugação. Para quantificar e caracterizar o perfil de polifenóis, os sumos foram purificados por Extracção de Fase Sólida (SPE) Coluna C18 para remover açúcares e outros compostos interferentes, analisados depois por Cromatografia de Alta Eficiência (HPLC) e Espetrometria de massa (ESI-MS). Os resultados mostram os principais polifenóis foram o ácido clorogénico e as procianidinas e que a temperatura leva a uma diminuição do teor de polifenóis, 1,081 ±0,130 mg/mL a 0,763 ±0,018 mg/mL, nos sumos clarificados, quanto aos sumos turvos apresentaram valores mais baixos, 0,470±0,025 mg/mL e 0,770±0,024 mg/mL. O menor teor em polifenóis poderia ser explicado pelo facto de os compostos de polifenóis estarem presos nos precipitados recolhidos por centrifugação. Assim, o aumento da velocidade diferencial da centrifugação parece resultar numa maior concentração de polifenóis solúveis. O menor teor em polifenóis poderia ser explicado pelos polifenóis estarem presos nos precipitados recolhidos por centrifugação. As análises em curso estão a explorar os polifenóis presentes nos precipitados.

Em conclusão, a filtração e as centrifugações podem afectar o teor de polifenóis. Os resultados sugerem que as matrizes de frutos de maçã podem oferecer um elevado conteúdo de compostos de polifenóis, dependendo do processo, e no final, o seu consumo pode contribuir para promover benefícios para a saúde.

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Propiedades nutricionales y bioactivas de la frambuesa roja Kweli® cultivada en Portugal

Matilde Rodrigues[1,2], Ana Luísa Vara[1], Jovana Petrović[3], Maria Inês Dias[1,2], Marina Soković[3], António Nogueira[1,2], Isabel C.F.R. Ferreira[1,2], José Pinela[1,2,*], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Institute for Biological Research "Siniša Stanković" – National Institute of Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia
**jpinela@ipb.pt*

La frambuesa roja (*Rubus idaeus* L.) es un alimento cada vez más popular en la dieta contemporánea debido a su frescura, características organolépticas y evidencias de propiedades saludables. Desde el punto de vista composicional, la frambuesa roja contiene vitaminas, minerales, fibra soluble, azúcares reductores, ácido cítrico y compuestos fenólicos [1]. Las antocianinas son de especial interés en esta fruta, ya que estos pigmentos le proporcionan el característico color rojo-púrpura y propiedades bioactivas [1,2]. La demanda de frambuesas ha aumentado considerablemente en Europa y América del Norte y, entre los cultivares existentes, Kweli® es uno de los más productivos y aptos para el cultivo en climas moderados y mediterráneos. Sobre este cultivar ya se han descrito altos niveles de elagitaninos, antocianinas y vitamina C y su contenido fenólico se ha correlacionado con propiedades antioxidantes [1,2]. Sin embargo, poco más se sabe sobre la composición nutricional de Kweli®. Por lo tanto, este trabajo se realizó para caracterizar la composición nutricional y química de este cultivar de frambuesa roja y evaluar su actividad antioxidante y antimicrobiana. Los frutos frescos en su madurez comercial fueron cosechados e inmediatamente liofilizados. Se determinó su composición proximal por los métodos oficiales de análisis de alimentos y se evaluaron las concentraciones de azúcares libres, ácidos orgánicos, tocoferoles y ácidos grasos mediante diferentes técnicas cromatográficas [3]. Se identificaron las antocianinas en un extracto hidroetanólico preparado por extracción sólido-líquido, que también se utilizó para evaluar las propiedades bioactivas [3]. La actividad antioxidante se evaluó mediante la inhibición del blanqueo del β-caroteno, de la formación de sustancias reactivas al ácido tiobarbitúrico (TBARS) y de la hemólisis oxidativa [3]. La actividad antimicrobiana se probó contra cepas bacterianas y fúngicas transmitidas por los alimentos mediante métodos de microdilución [3]. La humedad (~83%) y los hidratos de carbono (16,12%), de los cuales la fructosa (2,42%) y la glucosa (2,13%), fueron los principales componentes de la frambuesa roja, seguidos de las cenizas (0,66%) y las proteínas (0,18%). El contenido en grasa era bastante bajo y estaba compuesto principalmente por ácidos grasos insaturados (58%), con predominio del ácido oleico. También se detectaron niveles elevados de ácidos cítrico y ascórbico y tocoferoles. Las antocianinas cianidina-3-*O*-glucósido y cianidina-3-*O*-soforósido se identificaron en el extracto, que fue capaz de inhibir en cierta medida la formación de TBARS, la hemólisis oxidativa y el blanqueo del β-caroteno. Además, el extracto fue más eficaz que el aditivo alimentario E224 contra *Bacillus cereus*. Estos resultados destacan la calidad nutricional de la frambuesa roja y pueden ser útiles para completar las bases de datos de composición de alimentos. Por lo tanto, la inclusión de esta baya en la dieta diaria puede ser útil para obtener nutrientes y antioxidantes y aportar beneficios para la salud.

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Optimización de la extracción asistida por microondas de aceite de subproductos de pescado y evaluación de su calidad nutricional

Matilde Rodrigues[1,2], Beatriz de la Fuente[1,3], Cristina Caleja[1,2], André Almeida[4], Maria Inês Dias[1,2], José Pinela[1,2,*], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Preventive Medicine and Public Health, Food Science, Toxicology and Forensic Medicine Department, Faculty of Pharmacy, Universitat de València, Avda. Vicent Andrés Estellés, 46100 València, Spain
[4]ITS - Indústria Transformadora de Subprodutos S.A., Rua Padre Adriano, 61, 2660-119, Santo Antão do Tojal, Loures, Portugal
**jpinela@ipb.pt*

La industria pesquera produce anualmente grandes cantidades de subproductos de pescado, de los cuales, una pequeña parte se destina directamente para alimentación animal [1]. Debido a la presencia de compuestos liposolubles de alto valor añadido y al importante contenido en lípidos en algunos tejidos del pescado, el interés de la industria pesquera para producir aceite a partir de estos subproductos ha aumentado en los últimos años [1]. Sin embargo, los métodos convencionales de extracción de aceite de los alimentos pueden llevar mucho tiempo y ser poco atractivos para la industria. A pesar de que se han implementado tecnologías no convencionales para la extracción de algunos compuestos liposolubles de origen marino, su aplicación para recuperar aceite de pescado ha sido poco explorada [2]. Por lo tanto, este trabajo se llevó a cabo con el objetivo de optimizar la extracción asistida por microondas (EAM) de aceite de subproductos de pescado y comparar la eficiencia de este método innovador con la de la extracción tradicional Soxhlet (ES). Los subproductos de pescado suministrados por la industria procesadora fueron caracterizados y liofilizados. La EAM se llevó a cabo siguiendo un diseño de compuesto central que combina cinco niveles de tiempo de procesado (1-30 min), potencia de microondas (50-1000 W) y relación muestra/solvente (70-120 g/L). Además, se utilizó la metodología de superficie de respuesta para la optimización del proceso [3]. Para comparar y evaluar la eficiencia de la EAM, se realizó una ES durante 6 h con una relación muestra/solvente de 20 g/L [3]. El hexano fue el disolvente utilizado en ambos métodos. El rendimiento de aceite se determinó gravimétricamente y el perfil de ácidos grasos se analizó mediante cromatografía de gases con detección de ionización de llama tras un proceso de derivatización [3]. Posteriormente, los datos experimentales se ajustaron a una ecuación cuadrática y los modelos desarrollados se validaron estadísticamente en base a R^2 y R^2_{Adj} elevados y una falta de ajuste no significativa, entre otros criterios. El rendimiento de aceite fue significativamente afectado por las tres variables independientes mediante efectos lineales, cuadráticos y/o interactivos. La EAM permitió obtener un rendimiento de aceite de pescado (18,6±0,3%) similar al obtenido con la ES (18±1%), pero con tiempos de extracción inferiores a 20 min. Las condiciones óptimas de la EAM predichas por el modelo fueron validadas experimentalmente con éxito. La composición de ácidos grasos no se vio afectada por las variables del proceso, observándose un buen perfil nutricional debido al predominio de ácidos grasos insaturados respecto a ácidos grasos saturados, principalmente por los altos contenidos de ácido oleico (~32%) y ácido docosahexaenoico (~9,6%).

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ALM27

Delivery vehicles for resveratrol incorporation in bread

Andreia F. R. Silva [1], Mariana Monteiro [1], Rute Nunes [2,3], Ana Baião [2], Susana S. Braga [1], Bruno Sarmento [2,3,4],
Manuel A. Coimbra,[1] Artur M. S. Silva,[1] Susana M. Cardoso [1*]

[1] LAQV-REQUIMTE, Laboratório Associado para a Química Verde, Universidade de Aveiro, Aveiro, Portugal
[2] i3S, Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Porto, Portugal
[3] INEB, Instituto de Engenharia Biomédica, Universidade do Porto, Porto, Portugal
[4] CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde, Gandra, Portugal
**afrs@ua.pt*

The application of delivery systems for bioactive compounds is an innovative strategy in the food sector to ensure the compound's bioactivity. Cyclodextrins (CDs) have been extensively used to increase hydrophobic compounds' solubility by forming inclusion complexes [1]. Zein nanoparticles are a food-grade material that has been used to protect, deliver and improve molecules' bioavailability [2]. *Trans*-resveratrol (RSV) is a health promoter bioactive compound potentially used as a functional food ingredient but its application is limited by its low water solubility and easy conversion into its non-active *cis* isomer. This work intends to formulate a functional wheat bread using RSV complexed with γCD (γCD·RSV) and RSV-loaded zein nanoparticles (Npz-RSV) and evaluate their impact on RSV stability, antioxidant activity, bioaccessibility and bioavailability. Bread with free RSV was used as a positive control and plain bread was used as a negative control.

The γCD·RSV was obtained by mixing an equimolar amount of an aqueous solution of γCD with an ethanolic solution of RSV, freeze-drying and characterization by Fourier Transform Infrared Spectroscopy (FTIR), powder X-ray diffraction (PXRD) and thermogravimetry (TG). Npz-RSV were obtained by nanoprecipitation, dropwise of an ethanolic solution of zein and RSV into water (RSV loading of 13.9%) and characterized by light scattering for size and laser doppler electrophoresis for zeta potential. The bread was prepared with wheat flour, water, yeast, salt and supplemented with 0.5% of RSV in free form and γCD·RSV and Npz-RSV. The surface color was measured by CIElab parameters using a colorimeter and bread texture was estimated through a two-bite texture profile analysis on a texture analyzer. 0.5 g of each bread (milled) was extracted with 10 mL of 70% ethanol for 15 min, and the supernatant was used for RSV quantification in ultra-high-pressure liquid chromatography at 306 nm and antioxidant activity analysis through $ABTS^{\bullet+}$ radical, oxygen radical absorbance capacity (ORAC) and nitric oxide (NO). The Bioaccessibility of RSV was determined by *in vitro* digestion of fresh cooked bread and bioavailability through permeability studies in cell monolayer models [3].

FTIR and PXRD analyses confirmed the γCD·RSV formation, where shifts in the peaks of γ-CD·RSV relative to the RSV spectrum were observed, and TG proved its thermostability at working conditions. Npz-RSV presented 187 ± 7 nm in size and a 23.2 ± 1.0 mV zeta potential. γ-CD·RSV did not affect the bread color but increased bread hardness, while Npz-RSV increased the yellowness and put the texture less stiff. Bread extracts recovered 89.0%, 70.3% and 62.8% of RSV from RSV-bread, γCD·RSV-bread and Npz-RSV-bread, respectively. The lower RSV recovery from γ-CD·RSV-bread and Npz-RSV-bread could indicate some retention of RSV in bread, probably due to the interaction of CDs and Npz with the matrix. Bread extracts hold antioxidant activity due to RSV, but some pro-oxidant activity of components of bread matrices cannot be neglected, with the additional quenching effect of RSV-delivery vehicles on chemical groups of RSV to interact with radicals [4]. RSV bioaccessibility was promoted by γCD·RSV (about 40%), compared with the positive control and Npz-RSV, but its bioavailability was not improved. The use of delivery vehicles contributed to RSV protection and higher bioaccessibility; overall, bread matrice was also a suitable vehicle for RSV.

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Obtenção otimizada de extratos bioativos de casca de marmelo: Uma fonte alternativa de conservantes naturais

Alexis Pereira[1,2], Mikel Añibarro-Ortega[1,2], Ana Cirić[3], Marina Soković[3], António Nogueira[1,2], José Pinela,[1,2,*] Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia,
5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto
Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]University of Belgrade Institute for Biological Research "Siniša Stanković", 142 Bulevar despota Stefana,
Belgrade, Serbia
**jpinela@ipb.pt*

O marmelo (*Cydonia oblonga* M.) é um fruto amargo e adstringente utilizado sobretudo na produção de marmelada e outros produtos alimentares açucarados. De acordo com a Legislação Portuguesa [1], a marmelada é uma mistura homogénea e consistente obtida exclusivamente da cozedura do mesocarpo do marmelo com açúcares. Portanto, a produção industrial de marmelada implica o descarte da casca como um subproduto. No entanto, estudos anteriores indicam que a casca deste fruto possui compostos bioativos com propriedades antioxidantes e antimicrobianas e efeitos promotores de saúde [2-4]. Este estudo propõe assim a reinserção deste subproduto na cadeia de valor sob a forma de um conservante alimentar natural. Para otimização do processo de extração de compostos bioativos a partir desta matriz vegetal, foi implementado um desenho de composto central circunscrito de 20 pontos, combinando os efeitos dos fatores tempo (1–119 min), temperatura (25–94 °C) e proporção de etanol (0–100%). Como variáveis dependentes, foram considerados o rendimento das extrações, avaliado gravimetricamente, e os teores de compostos fenólicos e ácidos orgânicos, quantificados por HPLC-DAD-ESI/MS^n e UFLC-PDA, respetivamente [5]. Estas análises permitiram identificar vários compostos fenólicos, incluindo ácidos fenólicos, flavan-3-óis e flavonóis, e ácido málico, entre outras moléculas. Os dados quantitativos foram seguidamente ajustados a uma equação polinomial quadrática para obtenção de modelos teóricos, os quais foram validados estatisticamente e usados para determinar as condições ótimas de extração. Estas foram aplicadas experimentalmente e os extratos obtidos foram analisados quanto ao potencial conservante, através da avaliação da atividade antioxidante por ensaios *in vitro* e da atividade antimicrobiana por métodos de microdiluição [5]. Estes extratos apresentaram capacidade de inibir a peroxidação lipídica e de inibir o crescimento de fungos e bactérias associadas a contaminações alimentares, destacando-se em alguns aspetos comparativamente com aditivos alimentares usados como controlo positivo. Estes resultados destacam o potencial inexplorado da casca de marmelo para obtenção de extratos bioativos ricos em compostos fenólicos e ácido málico, os quais poderão ser usados pela indústria alimentar para incorporação em alimentos e bebidas.

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Bioprospecting sequential extraction to obtain valuable compounds from brown macroalgae *Fucus vesiculosus*

Ana R. Circuncisão[1*], Artur M. S. Silva[1], Manuel A. Coimbra[1], Susana M. Cardoso[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
**anarcircuncisao@ua.pt*

Marine macroalgae, commonly known as seaweeds, have recently attracted interest as a valuable source of key nutrients and bioactive compounds, as well as renewable feedstocks. In particular, brown macroalgae are recognized for their abundance in specific target compounds, including phlorotannins and fucoxanthin which are phenolics and carotenoids, respectively, as well as polysaccharides including fucoidans, laminarans and alginates. Notably, all these compounds have been shown promising bioactivities, thus making them attractive to be used as added-value ingredients in functional foods [1,2]. Nevertheless, the strong and unfamiliar seaweeds' taste and flavour limits its application as food ingredient, therefore using seaweeds extracts has been proposed as an alternative strategy to harvest their benefits [2]. Simultaneously, it is imperative to develop low-cost and sustainable extraction strategies to promote resources efficiency. In this line, the main objective of this work was to develop a holistic strategy to obtain economic-affordable extracts rich in specific target compounds from brown macroalgae *Fucus vesiculosus* to be potentially applied as added-value ingredients in functional foods.

Based on the optimization of different extraction parameters, two distinct sequential extraction approaches were developed, both employing conventional solid-liquid extractions and differing mostly in the first step: the first approach started with a cold water extraction, while food-grade ethanol was used in the second approach. The resulting macroalgae residues from both approaches were separately extracted with 70% EtOH in order to recover phenolics and pigments, following by hot water extraction to recover water-soluble polysaccharides and a precipitation with 2% $CaCl_2$ to recover alginates.

The results revealed that cold water extract (38%) had higher yields comparatively to EtOH extractions (9 – 18%) from both approaches. The use of coldwater at the start of the process allowed the recovery of water-soluble phlorotannins (0.2% dw), mannitol (5% dw) and branched laminarans (1.1% dw), while sequential 70% EtOH extraction yielded the highest fucoxanthin recovery (1.3% dw). Contrarily, the use of food-grade ethanol at the start of the process allowed the obtaining of phlorotannins-richer extracts (0.4% dw), but almost no fucoxanthin was detected. In addition, water- and hydroethanolic-soluble phlorotannins were tentatively characterized by HPLC-DAD-ESI-MS^n. The sequential extraction with hot water in the first approach allowed to obtain fucoidans-purer fractions, whereas fucoidans were co-extracted with laminarans when using the second approach. The amount of recovered calcium-alginates accounted for 2 to 4% dw and M/G ratios were determined. At the end of the extraction, both approaches resulted in a final residue that was still rich in alginates. Therefore, they were submitted to a commonly industrial extraction procedure which allowed to recover additional 6 to 9 % dw of alginates. Overall, this work allowed the development of a holistic extraction procedure to obtain economic-affordable brown macroalgae-rich extracts by using simple techniques and environmental-friendly solvents. The multiple obtained food-grade extracts rich in specific target compounds with bioactive potential open up opportunities for their application as ingredients in the formulation of new functional foods.

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Nutritional, chemical and bioactive characterization of *Peumus boldus* L.

Izamara de Oliveira[1,2,3], Ricardo C. Calhelha[1,2], Tiane Finimundy[1,2], Celestino Santos Buelga[3], Sandrina A. Heleno[1,2*], Lillian Barros[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, *Campus de Santa Apolónia, 5300-253 Bragança,* Portugal;
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Grupo de Investigación en Polifenoles (GIP-USAL), Facultad de Farmacia, Universidad de Salamanca, Spain;
*sheleno@ipb.pt

Peumus boldus L. (boldo) is known for its pharmacological effects associated with the chemical composition of its leaves. The objective of this work was to perform the nutritional, chemical and bioactive characterization of boldo leaves.

The nutritional profile (crude fat, protein, ash, fiber, and carbohydrates) was determined using AOAC methods [1], while free sugars were determined by HPLC-RI and fatty acids by GC-FID. Moreover, organic acids were determined by HPLC-DAD, tocopherols by HPLC-fluorescence, and phenolic compounds by HPLC-DAD-ESI/MS. Afterwards, a hydroethanolic extract was prepared by maceration (80:20 *v/v*, ethanol:water), and the antioxidant potential was evaluated using the thiobarbituric acid reactive substances (TBARS) assay; antimicrobial capacity using the microdilution method against pathogenic microorganisms; cytotoxicity against tumor and non-tumor cell lines using the sulforhodamine B assay, and anti-inflammatory potential using RAW cells. For the nutritional profile results, the highest values were obtained for carbohydrates (78 ± 1 g/100 g dw, of which 48.0 ± 0.2 g/100 g dw corresponded to fiber), followed by proteins (8.2 ± 0.5 g/100 g dw), ash (10.0 ± 0.9 g/100 g dw) and fat (4.24 ± 0. 06 g/100 g dw), having an energetic value of 285 ± 2 kcal. Glucose (6.82 ± 0.03 g/100 g dw), followed by fructose (2.70 ± 0.04 g/100 g dw) and sucrose (1.50 ± 0.10 g/100 g dw) were the detected sugars. Ten fatty acids were found, with three main compounds standing out, namely palmitic (29.56 ± 0.05 %), oleic (19 ± 5 %) and linolenic (17 ± 2 %) acids. Five organic acids were identified, highlighting oxalic (1.26 ± 0.04 g/100 g dw) and quinic (1.24 ± 0.05 g/100 g dw) acids. The vitamin E isoforms γ-tocopherol (15 ± 1 g/100 g dw) and α-tocopherol (5.2 ± 0.3 g/100 g dw) were the ones identified in boldo leaves. Seventeen phenolic compounds were detected, from which proanthocyanidins were the most prominent, especially a proanthocyanidin dimer (34.69 ± 0.91 mg/g), and two proanthocyanidin trimers, 1 (32.12 ± 0.75 mg/g) and 2 (18.59 ± 0.67 mg/g). For the antioxidant potential (TBARS), an EC_{50} of 36.8 ± 0.2 μg/mL was determined, and for the antimicrobial capacity, lower minimum inhibitory concentrations (MIC) were seen especially against the foodborne bacteria *Yersinia enterocolitica* (1.25 mg/mL) and *Staphylococcus aureus* (1.25 mg/mL), as well as the clinical isolates *E. coli* (2.5 mg/mL), *Morganella morganii* (2.5 mg/mL), *Enterococcus faecalis* (2.5 mg/mL) and methicillin-resistant *S. aureus* (2.5 mg/mL). Boldo leaves showed cytotoxicy against non-small lung carcinoma (71 ± 4 μg/mL), gastric adenocarcinoma (159 ± 12 μg/mL), and breast carcinoma (280 ± 9 μg/mL) cells. They also showed anti-inflammatory activity for macrophage cell line (RAW cells) at 145 ± 13 μg/mL. Thus, besides being rich in nutrients, *P. boldus* revealed the presence of bioactive compounds which can be used for future applications in the food, cosmetic and pharmaceutical industries.

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Antimicrobial activity of rosemary, eucalyptus and propolis individual and mixed extracts

Tebai Abir[1,2,3], **Izamara Oliveira**[1,2], **Soraia Falcão**[1,2], **Ines Ben Rejeb**[3], **Lillian Barros**[1,2], **Sandrina A. Heleno**[1,2*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal;
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] University of Carthage, National Institute of Applied Sciences and Technology (INSAT), LR05ES08 Laboratory of Microbial Ecology and Technology, Department of Biological and Chemical Engineering, BP 676, 1080 Tunis, Cedex, Tunisia
**sheleno@ipb.pt*

Preservative-free meals and the use of natural products as natural alternatives are becoming more popular as consumers become more aware of the potential health problems associated with artificial food preservatives. The current study focused on exploring the potential of plant extracts (rosemary and eucalyptus) and propolis, or their mixtures, to develop a highly bioactive formulation. Extracts were prepared individually and mixtures of eucalyptus/propolis, eucalyptus/rosemary, and rosemary/propolis using hydroethanolic extracts (80% ethanol) in different ratios of 50:50, 60:40, and 40:60, respectively., were also prepared. The selected matrices were prepared by two different maceration processes: i) 1 g of the sample was macerated in 30 mL of 80% hydroethanolic solution using magnetic stirring; ii) 1 g of sample in 10 mL of hydroethanolic solution was macerated in a water bath at 70°C, this being, the recommended protocol for extraction of phenolic compounds from propolis [1]. The extracts were further analyzed for their antimicrobial ability by microdilution method using pathogenic microorganisms. The individual extracts of rosemary and eucalyptus showed remarkably strong antibacterial activity against most bacterial strains, often equivalent to that obtained with the common antibiotic's streptomycin, methicillin, and ampicillin. Both mixtures, eucalyptus/rosemary (60:40) collected from maceration by magnetic stirring and eucalyptus/propolis (60:40) derived from maceration with water bath, showed the most promising results, with inhibition ability against all bacteria. As for the antifungal ability, no inhibition was obtained at the maximum tested concentration of 10 mg/mL.

In addition to these encouraging results for antimicrobial activity, further bioactivity assays will be performed to evaluate the properties of the different extracts.

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Chemical content and antioxidant activity variation during cherry development stages after application of biostimulants

Sílvia Afonso[1,*], Daniela Macedo[2], Ivo Oliveira[1], Anne S. Meyer[3], Berta Gonçalves[1]

[1] Centre for the Research and Technology for Agro-Environmental and Biological Sciences, CITAB, Institute for Innovation, Capacity Building and Sustainability of Agri-food Production, Inov4Agro, University of Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal.
[2] University of Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal.
[3] Technical University of Denmark, Department of Biotechnology and Biomedicine, DTU Building 221, DK-2800 Kgs. Lyngby, Denmark.
*safonso@utad.pt

In order to achieve maximum productivity and tree performance, while improving the nutritional value and quality of fruits, biostimulants have emerged as promising environmental-friendly products to promote the overall sustainability of production systems [1]. The application of seaweed extracts promotes an increase in the concentration of phenolic compounds, and antioxidant activity, and has positive effects on stress mitigation [2].

With excellent organoleptic properties, a high nutritional value, and recognized health-promoting properties, sweet cherries are a fruit of choice for consumers that are increasingly demanding and attentive to these issues [3]. In fact, this fruit is widely recognized, due to its biological activities, closely linked to its high content of phenolic compounds with antioxidant properties [4].

Little is known about the changes in the content of these health-promoting compounds during development of the sweet cherry as ripening advances, after the application of biostimulants.

Thus, this work intends to highlight the effect of the pre-harvest application of two concentrations of a seaweed-based biostimulant (0.30% (SW >) and 0.15% (SW <)) on the bioactive content (total phenolics, flavonoids and *o*-diphenols) and antioxidant traits (DPPH, FRAP, and ABTS) of sweet cherries fruits. Sweet cherries cv. *Lapins,* grafted on "Saint Lucia" rootstock, were collected from a commercial orchard, located in Resende, Northern Portugal. The treatments were foliar applied at three different phenological stages of fruit development (stages 77, 81, and 86 according to the BBCH scale). Sweet cherries were then harvested three days after each application. In order to achieve more accurate results, treatments were applied for three consecutive years (2019, 2020, and 2021). The results only refer to the first year of application and the last one. Overall, total phenolic content was higher in 2021, when in contrast to 2019 and it decreases as maturation of the fruit advances. The SW < treatment resulted in higher content of phenolics. The same decreasing trend with ripening that was found for total phenolics was also found for flavonoids and *o*-diphenols. Both flavonoids and *o*-diphenols contents increased in 2021, compared to 2019, with enhanced values when SW < treatment was applied. Regarding the antioxidant activity, an overall similar pattern can be observed in the two years, even though the equivalent activity is higher in 2021 with the application of the treatment of lower concentration.

These findings provide, not only information about the effect of biostimulant application on sweet cherry fruit, but also about its outcome during the different stages of fruit development, thus filling the gap in knowledge about the accumulation patterns of its health-promoting compounds.

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QUÍMICA AMBIENTAL Y SOSTENIBLE

Remoção de parabenos por processos Fenton e foto-Fenton

Ana R. Teixeira[1*], Nuno Jorge[1,2], Marco S. Lucas[1], José A. Peres[1]

[1] Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal

[2] Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Espanha

**ritamourateixeira@gmail.com*

Os parabenos são compostos derivados do ácido *p*-hidroxibenzóico com propriedades conservantes e antimicrobianas, muito aplicados nas indústrias cosmética, alimentar e farmacêutica [1,2]. A ampla utilização e a ineficácia das ETAR na remoção destes compostos, origina um aumento da sua concentração no meio aquático, tendo já sido detetada a sua presença em rios, águas subterrâneas, piscinas, águas de consumo, solos e organismos vivos [2]. Os parabenos atuam muitas vezes como disruptores endócrinos e estão associados a potenciais efeitos mutagénicos e cancerígenos. Neste sentido, é necessário adotar medidas para controlar e remover estes contaminantes emergentes dos ecossistemas [2]. Os Processos de Oxidação Avançados (POA) podem ser aplicados como alternativa ou complemento aos tratamentos tradicionais, para uma maior eficiência na remoção de compostos recalcitrantes dos efluentes, como são os parabenos [3].

O presente trabalho avaliou a eficiência de remoção do carbono orgânico dissolvido (COD) de uma solução mista de quatro parabenos - metilparabeno, etilparabeno, propilparabeno e butilparabeno (Fig. 1a), com uma $[COD]_i$ = 260 mg C/L. Estudou-se a aplicação do processo Fenton utilizando: (1) diversos catalisadores metálicos (sulfato ferroso, ferroceno, cloreto ferroso, cloreto férrico e nitrato de ferro III); (2) diferentes concentrações de catalisador (entre 0,026 e 6,71 mM); (3) variação de pH (natural ou 3,0) e (4) a influência de radiação UV (UV-C, UV-A e solar).

O melhor desempenho observou-se com o processo foto-Fenton UV-C (254 nm), tendo-se obtido uma redução de COD de 92,1% após 90 minutos de reação e 98,4% ao fim de 240 minutos (Fig. 1b).

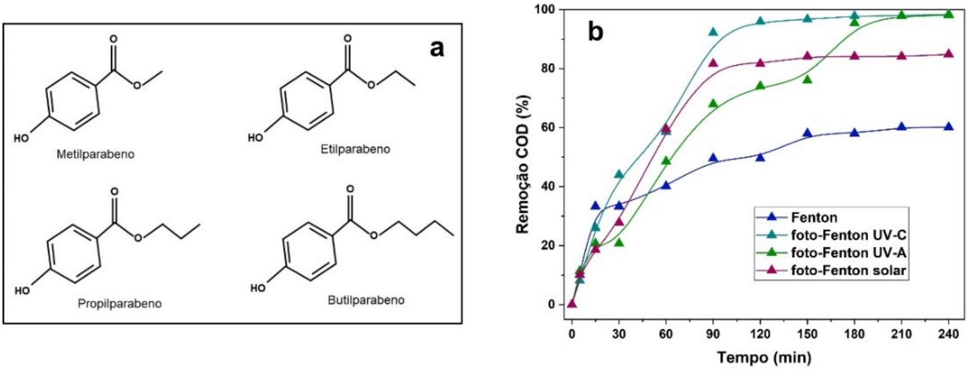

Fig.1. (a) Estrutura química dos parabenos estudados. **(b)** Evolução da remoção de COD ao longo da reação. Condições experimentais: pH = 3,0 [sulfato ferroso] = 4,0 mM e $[H_2O_2]$ = 68,0 mM (adição fracionada).

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Chemical contamination in “O Burgo” estuary (Galicia). Lithogenic and anthropogenic inputs to the sedimentary reservoir

Ricardo Prego[1,*], **Paula Álvarez-Iglesias**[2], **Begoña Quintana**[3], **Miguel Caetano**[4], **Carlos Vale**[5], **Miguel Ángel Álvarez-Vázquez**[1,6]

[1] Instituto de Investigaciones Marinas (CSIC), 36208 Vigo, Spain.
[2] SSADS-CACTI (University of Vigo), 36310, Vigo, Spain.
[3] Laboratorio de Radiaciones Ionizantes (University of Salamanca), 37008 Salamanca, Spain.
[4] Instituto Português do Mar e da Atmosfera, 1449-006 Lisboa, Portugal.
[5] CIIMAR (University of Porto), 4450-208 Matosinhos, Portugal
[6] Area de Geografía Física, GEAAT (University of Vigo), 32004 Ourense, Spain
**e-mail: prego@iim.csic.es*

Estuarine sediments constitute a biogeochemical reservoir where chemical trace elements from natural sources mix with a fraction generated from human activities. The study of contamination events from sediment cores, when coupled with geochronological techniques, is useful for reconstructing the temporal evolution of chemical contamination in estuaries and for calculating trace elements (TE) fluxes.

In particular, this can be applied to the “O Burgo” estuary in the Ria of “A Coruña”, where a phosphate fertilizers factory –currently dismantled- was settled and on which no study has been carried out until now. This estuary also has received sewage urban discharges. Then, it is hypothesized that the impact of this past anthropogenic activity, both urban and industrial, should be recorded in its estuarine sedimentary record. So, the rise and fall of these kind of anthropogenic pressures are addressed from three key questions: (i) identifying the chemical contamination in these sediments; (ii) temporally framing the contamination events by their chemical imprint on sediments; and (iii) defining the current situation by quantifying the lithogenic and anthropogenic fluxes to the sediment reservoir.

In order to achieve these three objectives, one sediment core of 51 cm long was taken with a hand-driven Gouge Augers Sampler (43,31394°N, -8,35930°W) in the intertidal muddy area of this estuary. ^{210}Pb, ^{214}Pb and ^{137}Cs activities were measured by low-level background gamma-ray spectrometry, and the Constant Rate of Supply model was applied for core dating (recovered sediments span the last 76±13 years). Major and trace elements were analysed by FAAS (Al, Ca and Fe), ETAAS (Hg) and ICP-MS (As, Cd, Co, Cr, Cu, lanthanoids -except Pm-, Mn, Mo, Ni, Pb, Th, U, V, Y and Zn). In addition, particulate organic matter proxies (C and N) were determined using an elemental CNH analyser.

Elemental depth profiles showed high organic matter contents in the first 13 cm (3.2-4.0% of POC, and 0.25-0.36% of PON), while four differenced patterns were differentiated for trace elements presented in the studied sediment core: (a) Co and Mn contents slightly varied (12.4±0.7 mgCo·kg^{-1}, and 377±26 mgMn·kg^{-1}); (b) Cr, Ni and V contents were relatively constant (41±4 mgCr·kg^{-1}, 20±2 mgNi·kg^{-1} and 65±5 mgV·kg^{-1}) but exhibited one peak at 27 cm depth, and an isolated low value at 37 cm; (c) As, Cd, Cu, Hg, Pb and Zn showed the highest values in the middle-core part (23-37 cm) reaching up to 1.54 mgCd·kg^{-1}, 143 mgCu·kg^{-1}, 4.21 mgHg·kg^{-1}, 279 mgPb·kg^{-1} and 786 mgZn·kg^{-1}; (d) Ln, Th, U and Y exhibited similar trends with little content changes (8.9±1.6 mgTh·kg^{-1}, 4.7±0.7 mgU·kg^{-1}, 18.0±1.4 mgY·kg^{-1} and 126±13 mgLn·kg^{-1}) and a small peak at 13 cm depth, as occurred with Al and Fe.

Since the 1930s, Hg contents increased up to the year 1964 (4.2 mg·kg^{-1}), then decreased slightly until 1975 and markedly from 1982 to 2012 (0.6 mg·kg^{-1}). Trends of Cd, Cu, Pb and Zn were similar. Contamination before 1985 was very high by Hg and Pb, and severe by As, Cd, Cu and Zn. This contamination coincides temporarily with the phosphate fertilizers factory operation -installed in 1932 and closed in 1989-, settled in the “O Burgo” estuary shoreline. Sediment accumulation rates (and organic matter fluxes) increased during two different periods: before (5.3±1.0 mm·yr^{-1}) and after 1985 (7.8±2.0 mm·yr^{-1}), related to the Mero River damming and building construction on the estuary banks.

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Combination of coagulation-flocculation-decantation with Fenton-based processes for agro-industrial wastewater treatment

Nuno Jorge[1,2 *], Ana R. Teixeira[2], Marco S. Lucas[2] and José A. Peres[2]

[1]Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Spain
[2]Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
** njorge@uvigo.es*

Agro-industrial wastewaters are attracting a lot of attention. Wastewaters generated by the processing of elderberry, olives and grapes are known for containing compounds such as polyphenols, organic acids, flavonoids, oils and greases, which together with high flows and seasonality lead to a limited application of conventional treatment technologies. An improper wastewater discharge in the ecosystems will represent a threat to all living forms [1,2].

Wine production generates large volumes of wastewater due to the wash and disinfection of all the equipment from the winery, such as the presses used for crushing the grapes, fermentation tanks, and barrels. The aim of this work is the treatment of winery wastewater (WW) by different methodologies: (1) coagulation–flocculation–decantation (CFD), (2) Fenton-based processes, and (3) CFD combined with Fenton-based processes.

The CFD process was performed using an organic coagulant derived from leaves of *Acacia dealbata Link*. The pH was varied from 3.0 to 11.0 and the ratio of leaves powder (LP):dissolved organic carbon (DOC) varied from 0.25:1 to 5:1 (w/w). Under the best operational conditions (pH = 3.0, DOC = 400 mg C/L, LP:DOC ratio 0.5:1, V = 500 mL, temperature 298 K, fast mix 150 rpm/3 min, slow mix 20 rpm/20 min, sedimentation time 12 h) it was observed a DOC and total polyphenols (TPh) removal of 18.2 and 35.8%, respectively.

To complement the CFD process, it were tested several Fenton-based processes (FBP). Fenton, Fenton-like and heterogeneous Fenton processes revealed a reduced removal of WW organic matter. Therefore, UV-C radiation was added to the Fenton-based processes, being reached a DOC removal of 70.3, 51.1 and 54.2%, respectively. The combination of CFD with FBP reached 98.2, 96.2 and 95.4% DOC removal, respectively and 99% TPh removal. The final values of COD, BOD_5 and TSS reached the values set by the Portuguese Law, and so the water can be used for irrigation. The energy efficiency analysis to the FBPs showed that application of CFD increased the energy efficiency of the UV-C system and reduces the treatment costs.

Finally, the sludge generated in the CFD process was tested as fertilizer. The germination of cucumber and radish seeds was assessed and results showed radicular growth and a germination index > 80%, thus the sludge can be reused as fertilizer.

Based in these results, the combination of CFD with FBPs allows the treatment of WW and its reuse for irrigation. In addition, *Acacia dealbata Link* leaves powder is an efficient coagulant and its sludge can be reused as soil fertilizer.

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AMB04

Treatment of a winery wastewater by a peroxymonosulfate/cobalt/ UV system

Nuno Jorge[1,2*], Ana R. Teixeira[2], Marco S. Lucas[2] and José A. Peres[2]

[1]Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitário de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Spain
[2]Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
** njorge@uvigo.es*

The winery wastewater (WW) is generated from the rinsing and destemming harvested grapes, washing barrels or transport equipment, pressing grapes and the accumulation of must/wine losses in the waste stream. However, the inefficient management of WW by the wine cellars is imprinting an unsustainable trademark on the global production of wine [1]. Considering the low biodegradability inherent to this type of wastewater, a chemical treatment approach should be studied to remove the recalcitrant organic matter. Sulfate radical advanced oxidation processes (SR-AOPs) appears as an efficient solution. The aim and novelty of this work was to create a statistical design to evaluate the best SR-AOPs to treat the WW. The goal is to reach the Portuguese legal values for wastewater discharge and promote the treated wastewater reuse. Considering the low information regarding WW treatment by sulfate radicals, a response surface methodology (RSM) Box-Behnken design was used in a WW with the following variables: PMS (0 – 10 mM), Co^{2+} (0 – 5 mM) and radiation (dark, UV-A). In the RSM, 15 experiments were performed. The results showed that among the different SR-AOPs applied, the PMS/Co^{2+}/UV-A system revealed to be the most efficient, and the system could achieve the maximum performance with PMS (5.9 mM) and Co^{2+} (5.0 mM). These conditions were optimized changing the pH (3.0 – 11.0), temperature (298 – 363 K), catalyst type and manner of addition of reagents, in a WW with a COD of 4925 mg O_2/L. The results showed that under the best operational conditions (pH = 6.0, temperature = 343 K, PMS (multiple addition), Co^{2+} (multiple addition) it was achieved a COD removal of 82.3%. The results fit into a pseudo first-order kinetic rate [2] and them a chart ln *k* vs 1/T (Arrhenius equation), revealed an activation energy of 16.07 ± 0.58 kJ mol^{-1} required to activate the PMS and generate sulfate radicals ($SO_4^{\bullet -}$). Afterwards, different sources of radiation (UV-A, UV-C and ultrasound (US)) were evaluated. The results showed a COD removal of 82.3, 76.0 and 52.2%, respectively. Clearly, the UV-A and UV-C had a higher effect in the conversion of PMS regarding US. The total polyphenols showed a near complete reduction with application of all radiation sources, which could indicate that these treatments are efficient in the breaking of aromatic compounds. The average oxidation state (AOS) and carbon oxidation state (COS) showed a considerable increase after the 240 min of reaction, which was consistent with the high reduction of organic carbon. The electric energy per order (E_{EO}) was evaluated and results showed higher consumption with application of US (12.8 kWh/ g COD) in comparison with UV-A and UV-C (0.173 and 0.423 kWh/ g COD, respectively). Considering the reagents cost and price of electricity, it was estimated a cost of 0.015, 0.035 and 1.03 €/g COD, for UV-A, UV-C and US systems. Considering these results, the RSM model revealed to be an efficient strategy to evaluate the best operational conditions. Finally, it is possible to conclude that PMS/Co^{2+} with UV-A or UV-C achieves a COD ≈ 1000 mg O_2/L, allowing the WW discharged in a municipal sewage network. Thus, PMS/Co^{2+}/UV could be an efficient and economically competitive process to treat WW.

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Determinación de normalizadores para elementos traza en el sedimento del continuum afluente-río-estuario-ría (Ulla-Arousa, Galicia)

Gonzalo Farinango[1,*], **Miguel Ángel Álvarez-Vázquez**[2], **Ricardo Prego**[1]

[1] Instituto de Investigaciones Marinas (CSIC), 36208 Vigo, España.
[2] Área de Geografía Física, GEAAT (Universidade de Vigo), 32004 Ourense, España.
* *gfarinango@iim.csic.es*

La estimación de los contenidos naturales de elementos traza en el sedimento es un paso crítico para cualquier evaluación de la contaminación. La comparación, ampliamente utilizada, en base a referencias globales o regionales supone una herramienta rápida y útil como enfoque exploratorio.

Sin embargo, por una parte, no tiene en cuenta las anomalías locales atribuibles a la variabilidad circunscrita a la litología. Por otra parte, cuando se considera la interfase tierra-océano, existe una variedad de ambientes sedimentarios con sus complejidades particulares, es decir, ríos sobre roca, ríos aluviales, estuarios, áreas costero-oceánicas.

Se puede plantear una pregunta científica: ¿Es posible aplicar un enfoque único a toda el área desde los cauces de cabecera hasta el océano?

Para dar una respuesta, se aplicaron las técnicas de estimación de niveles de fondo
-- univariante: a) límites de Tukey, b) gráficos de probabilidad normal;
-- bivariante: c) regresión de mínimos cuadrados.

Mientras que para determinar enriquecimientos se emplearon los índices Igeo (*geoaccumulation index*) y LEFs (*local enrichment factors*).

El estudio parte de 78 muestras de sedimentos superficiales recogidos en la cuenca hidrográfica del río Ulla (afluentes Lañas, Brandelos, Deza, Liñares y Sar), en el cauce principal del curso medio y bajo del río Ulla (desde el embalse de Portodemouros hasta Herbón), en el estuario del Ulla (Padrón-Carril) y en la zona interna-media de la ría de Arousa. Este continuum cubre tres dominios principales: continental (n=30), estuarino (n=12) y costero-oceánico (n=36) y una variedad de diferentes litologías. Como elementos de referencia se han seleccionado tres metales, aluminio, hierro y uranio, los cuales se aplican a dos contaminantes típicos, un metal, el plomo, y un metaloide, el arsénico.

Todos los métodos produjeron resultados parecidos en la estimación de fondo con un promedio de 14-17 $\text{mgAs}\cdot\text{kg}^{-1}$ y 31-36 $\text{mgPb}\cdot\text{kg}^{-1}$ y una dispersión similar para ambos, calculada como desviación estándar relativa, de alrededor de 24-43 %. Los contenidos de As y Pb en toda el área se hallan enriquecidos si se relacionan con la referencia global de la corteza continental superior [1], al igual que con la referencia regional [2]. Sin embargo, cuando se estiman los valores de fondo a nivel local, los enriquecimientos se localizan en áreas concretas. Las técnicas bivariadas presentan como ventaja un mejor ajuste para la estimación del nivel de fondo. Es destacable que el uso del aluminio, elemento de referencia muy utilizado, funciona peor en muestras de cabeceras (ríos sobre roca). El uranio, probablemente debido a su vinculación con los granitos, ha presentado en este caso particular un buen potencial como elemento de referencia para toda el área (desde las cabeceras continentales hasta el dominio oceánico). En consecuencia, ninguna técnica de estimación de fondo debe aplicarse automáticamente antes de ser probada empíricamente.

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Vine-canes-based extracts as antioxidants for biodiesel production: A Life Cycle Assessment study

E.Surra[1], O. Dorosh[1], M.Eusébio[2], M.M.Moreira[1], A.F.Peixoto[3], Luís M. N. B. F. Santos[4], C. Freire[3], C. Delerue-Matos[1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Inst. Politécnico do Porto, Porto, Portugal
[2] REQUIMTE/LAQV, Dep. Química *e Bioquímica*, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal
[3]REQUIMTE/LAQV, Dep. Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Porto, Portugal
[4]CIQUP, IMS -Institute for Molecular Sciences, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal
**elena.surra@graq.isep.ipp.pt*

Biodiesel is a renewable fuel produced from edible and non-edible vegetable oils, recycled waste vegetable oils, and animal fats, and it is susceptible to oxidation and rancidity during storage [1]. The commercial biodiesel oxidative stability, required by EN 14112, is commonly guaranteed by non-renewable fossil-based antioxidants, as butylhydroxytoluene (BHT) and blends. Vine canes-based (VC) extracts, rich in phenolic compounds [2], can be considered a promising sustainable alternative to typical synthetic additives.

The main goal of this work was to evaluate, in an early stage of development, the environmental advantages of the novel VC antioxidant extract produced by Subcritical Water Extraction (SWE) when compared to the commercial BHT through the Life Cycle Analysis (LCA) methodology. The LCA was developed hypothesizing: i) the production of a VC-based biodiesel additive at an industrial plant capable to process all the VC residues harvested in a 50 ha Portuguese vineyard; ii) the inclusion of an energy integration step in the plant design, which is able to reduce heat demand for final extract drying; iii) the reuse of the residual hydrochar from SWE, obtained after recovering antioxidant extract, as precursor for activated carbons (AC) production.

The environmental impacts associated with the production process of VC-based antioxidant show that this novel antioxidant is environmentally competitive with BHT up to its final drying in most of the categories of impact, with special regard to Global Warming, Fossil Resource Scarcity, Land Use, either hydrochar is landfilled, or used as precursors for AC production (ReCipe2016, MidPoint level). At EndPoint Level, dried VC extracts provided lower environmental impacts in Human Health, Ecosystem and Resources categories of impact than commercial BHT. However, when the novel VC extract is dissolved into benzyl alcohol, to favor its incorporation into biodiesel, the type and the amount of the solvent required can cut off the environmental benefits associated with VC antioxidant production when compared to BHT. The valorisation of generated hydrochar as precursor for AC allows to obtain additional environmental credits, suggesting that the valorisation of hydrochar is environmentally recommended.

This preliminary simulation provides fundamental information able to drive successive research steps, which must be focused on finding sustainable alternative solvents for solubilizing dried VC extract, as well as on reducing the amount of solvent to achieve the most favorable and sustainable solution.

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Removal of perfluoroalkylated substances (PFAS) with a broad spectrum of alkyl chain lengths (C1-C13) using a boron-doped diamond electrode and real aqueous matrices

Javier López-Vázquez[1*], Francisca C. Moreira[2,3], Carla S. Santos[2,3], Rosa Montes[1], Rosario Rodil[1], José Benito Quintana[1], Vítor J.P. Vilar[2,3]

[1]Department of Analytical Chemistry, Institute of Research on Chemical and Biological Analysis (IAQBUS), Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain.
[2]LSRE-LCM – Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
[3]ALiCE – Associate Laboratory in Chemical Engineering, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
*j.lopez.vazquez@usc.es

Poly- and perfluoroalkyl substances (PFAS) have been manufactured for many years for industrial and domestic applications due to their physico-chemical properties. There are more than 4700 PFAS in the global market, and the number is continuously growing due to the constant development of new PFAS-like chemicals [1]. PFAS resist hydrolysis and photolysis, and are not easily biodegraded, making them persistent in the environment, even being named “forever chemicals” [1]. Several studies have concluded that PFAS affect the immune system in humans, increase serum cholesterol concentrations, induce weight loss in neonates, or even affect the response to vaccines [2]. Hence, the European Union (EU) limited the presence of 20 PFAS (C4-C13) in water intended for human consumption by the 2020/2184/EU Directive. Besides, this directive intends to ban any PFAS (besides those 20) in the upcoming years. Conventional treatments are ineffective in their removal, and thus new technologies shall be developed to cope with this global threat to human health.

The present work aims at assessing the performance of the anodic oxidation (AO) process using a boron-doped diamond (BDD) anode for the removal of PFAS from aqueous matrices. Both the nowadays regulated group of PFAS under Directive 2020/2184/EU (C4-C13) and the ultrashort-chain PFAS (C1-C3) [3] were investigated (24 PFAS in total). The effect of the aqueous matrix was assessed by applying five different matrices – ultrapure water, drinking water, urban wastewater after secondary treatment, reverse osmosis and nanofiltration concentrates from urban wastewater treatment tertiary treatment. Low content of 0.2 µg/L of each PFAS was applied in all these matrices and experiments were conducted at different current densities. PFAS with carboxylic moieties proved to be more easily degraded than those with sulfonic ones. Whereas the former PFAS were (almost) completely removed, the removal of the latter ones greatly varied with the carbon-chain length, from less than 10% for C1 to complete removal for C8. The presence of other species in real matrices affected the efficiency of PFAS removal, but not hindered the use of the AO process.

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AMB08

A Sustainable Methodology for the Preparation of HIV Protease Inhibitors to Tackle Viral Resistance

Xavier Cruz Correia[1], Ivo E. Sampaio-Dias[1,*]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
**idias@fc.up.pt*

The most effective therapy currently available to fight infections by the human immunodeficiency virus (HIV) is the highly active antiretroviral therapy (HAART).[1] This therapy successfully suppresses the replication of the virus, resulting in reduced morbidity and mortality associated with HIV infection, as well as improving the lifespan of patients.[1] Protease inhibitors (PIs), such as Amprenavir and Darunavir, are a class of antiretroviral drugs used in HAART that prevent the maturation of viral particles by inhibiting the enzyme protease and thus suppressing the restructuration of viral proteins.[1] However, the crescent use of PIs in chronic therapy induces mutations in the virus, resulting in the development of drug-resistant strands.[2] As such, there is a constant necessity for the discovery of novel antiretroviral pharmaceuticals to fight resistant strands of the virus.[2]

A common research approach in this regard is the design and synthesis of Amprenavir/Darunavir analogues by the replacement of the P2 group, conserving the (*R*)-(hydroxyethyl)sulfonamide structural motif (P1, P1’, and P2’ sites),[3] which is relevant for the pharmacological properties of these compounds (**Fig. 1**). In the literature, different methodologies are reported for the synthesis of the (*R*)-(hydroxyethyl)sulfonamides, the majority of them uses disconnective approaches, hazardous solvents, and are limited to small academic scale synthesis.

In this work, an innovative and practical multi-gram one-pot methodology is presented for the preparation of the (*R*)-(hydroxyethyl)sulfonamide structural motif. The key steps of this novel protocol are the preparation of the amino alcohol precursor in ethanol as the solvent and the sulfonamide synthesis in an aqueous medium, offering high global yields (>91%) and chemical purity (>98%, HPLC). Moreover, this methodology avoids chromatography techniques, thus offering a more sustainable approach for the preparation of this structural motif, boosting the HIV drug research of structure-related Amprenavir and Darunavir analogues.

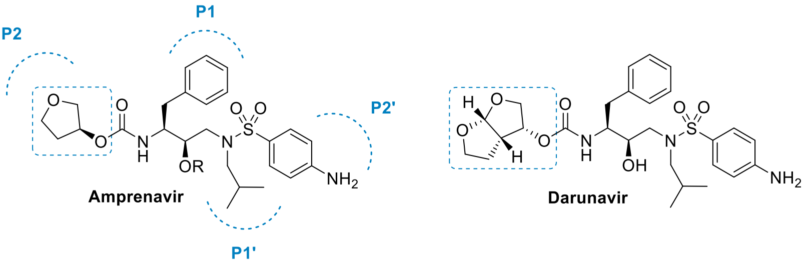

Fig.1. Structures of highly active HIV protease inhibitors Amprenavir and Darunavir, highlighting the conserved (*R*)-(hydroxyethyl)sulfonamide structural motif (P1, P1’, and P2’ sites).

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Controlled thermal degradation of Polyoxometalate@Zeolitic Imidazolate Framework composites towards novel oxidation catalysts

Rui G. Faria[1,*], Olívia S.G.P. Soares[2], Dinis F. Silva[1], Salete Balula[1], Luís Cunha-Silva[1]

[1]LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, Porto, Portugal
[2]LSRE-LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Portugal
**up201202396@fc.up.pt*

Despite recent strides towards a green energy transition, fossil fuels are still the only viable option for the maritime and air transport sectors, thus, steps must be taken in order to minimize their environmental impact.

Oxidative desulfurization (ODS) is a promising sustainable and cost-effective method to remove environmentally harmful sulfur compounds from fuels. The viability and potential applicability of this method at an industrial level is heavily dependent of the research and development of adequate catalysts, combining thermal, mechanical and chemical stability with remarkable activity.[1]

Polyoxometalates (POMs) have been demonstrated as excelent homogeneous catalysts towards ODS [2], and can be used in tandem with environmentally sustainable oxidants such as hydrogen peroxide, resulting in excellent desulfurization efficiencies under low temperature and pressure conditions, however, their solubility presents a disadvantage towards catalyst recycling and reuse. POMs can be heterogeneized with various different approaches, chief among them being the immobilization in support matrices such as Metal-Organic Frameworks.

MOFs are inorganic-organic hybrid crystalline 3D coordination polymers characterized by possessing the aforementioned stability properties, which can reveal high synergistic effects with POMs in oxidative catalytic systems due to their porous systems acting as nanoreactors [3].

Porous POM@Zeolitic Imidazolate Frameworks (ZIF, a family of MOFs) composites were prepared under an energetically sustainable bottle-around-the-ship approach at room temperature and pressure, aiming for the preparation of novel MOF-based composite materials. The prepared heterogeneous catalysts were also subjected to controlled thermal degradation, with the goal of altering their porous structure and promoting higher catalytic efficiencies. The obtained materials were characterized by FTIR, XRD, SEM/EDS, TGA, ICP-OES and N_2 adsorption isotherms and were applied as heterogeneous catalysts for ODS processes in model fuels. PMo_{12}@ZIF-8 attained the oxidation of 89% of the sulfur content in the MF after just 60 minutes, but its catalytical activity progressively decreased over the following cycles. Controlled termal degradation (CTM) of this composite at temperatures above 500 ^oC increased its activity (100% sulfur oxidation) and also made it reusable for at least 5 subsequent cycles with no loss of activity. Remarkably, CTM also revealed to be a useful strategy towards the activation of catalysts. The PMo_{12}@ZIF-67 composite, a previously inactive catalyst for ODS, became active after thermal treatment at 500 ^oC, and was used in 5 consecutive cycles with no loss of activity.

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Biomass-based materials for estrogens adsorption from water: production methods and their characterization

Eduardo C. Milani[1,2,3,*], **Maraísa L. Menezes**[3], **Jose L. Díaz de Tuesta**[1,2,4], **António E. Ribeiro**[1,2], **Paulo Brito**[1,2], **Ana Queiroz**[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] Universidade Tecnológica Federal do Paraná (UTFPR-AP), 86812-460 Apucarana, PR, Brasil
[4] Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Spain
*edurigueerick@gmail.com

Activated carbons (ACs) are low-cost carbonaceous materials with a high surface area ranging from 500 to 3000 m^2/g. ACs are produced by pyrolysis that consists of the combustion of organic matter above 500 °C in the absence of oxygen, to have the breaking of carbonic bonds and formation of porosity in the material. ACs are also undergo an activation process in order to increase its adsorption performance. Activation can be performed only by physical treatment, in which the organic material is thermal treated with an atmosphere of air, CO_2, and water vapor, or also by applying some chemical treatments using generally, strong acids, chloride salts or strong bases [1, 2]. As carbon source for ACs preparation, many precursors have been tested, mainly biomass wastes (olive stones, rice husk, coconut shell, among others) [2]. According to the Instituto Nacional de Estatística (INE), in 2021 Portugal produced more than 1.3 million tons of olives and it is estimated that more than 500,000 tons of residues were generated per year [3]. This work aims to investigate different production methods of ACs from olive stones change and their effects on the characteristics of the resultant adsorbents.

From the olive stone, five different materials were produced, namely (i) powdered olive stone, (ii) pyrolyzed at 800°C for 1h, with a heating rate of 10°C/min with N_2 flow of 20 cm^3/min, (iii) carbonized at 500°C for 1.5h with a heating rate of 10°C/min in a sealed crucible, (iv) chemical activated using acid phosphoric acid and (v) chemical activated with sodium hydroxide. The carbonization yield was determined, as well as the main physicochemical properties of ACs, such as the particle size frequency distribution of powdered raw-material, FTIR analysis and pH at point of zero charge.

The olive stone, after milling, had a predominant diameter of 188 µm, representing an average Sauter diameter of 162.4 µm. The moisture was 12.13% ± 0.08 and the ash content was 1.09% ±0.08. The carbon production method significantly influences the carbonization yield, acid activation was the method that allowed the highest yield (57.45%). The adsorbent's production method also has a significant impact on the adsorbents' pH_{PZC}, which is shown by the fact that the acid activation provides the material with the lowest pH_{PZC} (3.84).

The olive stone raw-material shows an important potential to be used on the production of activated carbons with high carbonization yields. Surface area, pore size, thermogravimetric analysis, and adsorption performance assays are under study.

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Green Chemistry in the Pharmaceutical Industry

Constantino Coelho[1], **Mafalda C. Sarraguça**[1,*]

[1]LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy,
Porto University, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
mafalda.cruz@ff.up.pt

Creating a safer, greener, and sustainable world is a challenge that all of us should undertake. The constant global increasing population and necessities, the increasing production requirement, the increasing consumption per capita, challenges the way we produce, create, and evolve, creating a profound footprint on the environment.

The pharmaceutical industry represents a big part of our evolution, creating new ways to make the humanity prosper through better health conditions, however its environmental impact is enormous. The production and use of pharmaceuticals cause high CO_2 emissions (52 Mtons in 2015, which is more than the automotive industry), contaminations of soils, biota, and water, and even danger to human health through carcinogenic impurities [1].

Green Chemistry represents a new way of making chemistry, environmentally friendly and advantageous for the evolution of chemical industry. In 1991, Paul Anastas used the term Green Chemistry for the first time, when he was integrating a program for the development of sustainable chemistry and chemistry technology for the industry, requested by the United States Environmental Protection Agency (USEPA), although, it was only in 1999 that Anastas defined and created the full concept of Green Chemistry [2]. Green chemistry is based on twelve principles, Prevention, Atom Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstocks, Reduce Derivatives, Catalysis, Real-time analysis for Pollution Prevention, and Inherently Safer Chemistry for Accident Prevention [3,4]. Beyond that, the term green chemistry is also referred as sustainable chemistry, environmental benign chemistry, atom economy or clean chemistry. As the years went through, Green Chemistry has turned itself more relevant to the industry, and Paul Anastas and his follower John Warner were the ones who most invested in the area, describing green chemistry as an environmental benign alternative to hazardous chemicals and processes, thus, promoting pollution prevention for the industry [5, 6].

In this work, greener solutions for the pharmaceutical field and industry based on the twelve principles of green chemistry are overview, from the use of greener solvents such as Deep Eutectic Solvents (DESs), Ionic Liquids (ILs), and Supercritical Fluids (SCFs), to lesser waste methods such as Catalysis and Mechanochemical methods. The objective of this work is to show greener roots for the pharmaceutical (and not only) industry to employ for an environmental safer and sustainable industry.

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Predicting DDT past and future contamination from a local source with a new gridded dynamic multimedia fate model

Parisa Falakdin[1*], Elisa Terzaghi[1], Giuseppe Raspa[2], and Antonio Di Guardo[1]

[1]Department of Science and High Technology (DiSAT), University of Insubria, via Valleggio 11, 22100 Como CO, Italy
[2]Department of Chemical Engineering, Materials, and Environment, Rome "La Sapienza" University, Via Eudossiana 18, 00184 Rome, RM, Ital
** E-mail contact: pfalakdin@uninsubria.it*

The relatively recent DDTs contamination of Lake Maggiore (Italy) offers an important experimental opportunity to study the release of DDTs from the soil. The high DDTs concentrations, discovered in 1996 in many fish species, caused the ban on fish consumption. DDTs were produced by a chemical company located in a subalpine valley (Ossola valley), and ended up in the Toce River, a tributary of Lake Maggiore. In the area surrounding the chemical plant, high DDTs concentrations in soil and vegetation were found after subsequent investigations. The quantification of the release from contaminated soil and the following migration towards downwind areas, deposition to the soil, and further evaporation plays an important role in understanding future DDTs trends in soil and the atmosphere. In order to study this phenomenon, soil and vegetation from Ossola Valley were monitored. The concentration values obtained, allowed to reconstruct the contamination gradient in the valley and were used to develop and calibrate a spatially resolved multimedia fugacity model. In this work, it is also described the development of a new grid modelling approach to survey the effect of spatial variation in environmental conditions on the distribution of chemicals at a local scale. A dynamic multiple box version of an existing multimedia box model (SoilPlusVeg) [1] is developed to account for the effect of wind speed and wind direction on the fate and transport of chemicals towards different compartments and geographical locations. The grid-based box model [2] consists of a user-defined number of connected cells where each cell represents a SoilPlusVeg model unit. Hourly meteorological data such as rainfall, temperature, wind velocity, and direction as well as the height of two dynamic air compartments are incorporated into the model. The connection between the cells is through advective flows of air. The model accounts for spatial and temporal dynamicity of environmental characteristics and simulates the fate and transport of chemicals on local to regional scales. The dynamic emission of DDTs from the highly contaminated soil in the vicinity of the chemical plant to the air for 100 years (from 1948 to 2048) was estimated and utilized for the simulation. The results obtained allowed to understand the temporal and spatial pattern of DDTs contamination and its potential contribution as a source potentially affecting sites at larger distances.

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Evaluation of activated carbon obtained from olive stones for the removal of sertraline from waters

<u>M.B. Belgacem</u>[1,2], A.E. Ribeiro[1,2], A. Queiroz[1,2], P. Brito[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

E-mail: mohamedbenbelgacem14@gmail.com

The presence of pharmaceutical drugs, their metabolites and degradation products in the environment requires significant research and monitoring studies to assess the potential risks to human health and to the ecosystem. Due to the extremely low concentrations of these chemicals in the environment in the trace levels of μg/L or even ng/L the removal processes must be optimized in order to make them easier, quicker, less expensive, and more environmentally friendly than traditional techniques [1]. Many of these substances, including hormones, antidepressants, analgesics, antibiotics, and anti-inflammatories, among others, are heavily medical prescribed around the world to treat the most prevalent illnesses associated with modern society. Sertraline belongs to the pharmaceutical class of anti-depressant and is intensively used worldwide to treat severe cases of depression. According to recent studies, several active principles from this family of pharmaceutical drugs, despite being at very low levels of concentration in water, can have a variety of harmful side effects in the environment's flora and fauna in addition to the potential risk of underground water contamination later used for animal or even human consumption [2-4].

This work will present the main experimental results for the removal of sertraline from water by adsorption using activated carbon obtained from olive stones. The activated carbon material was obtained from olive stones, by powdering the granulated olive stones to a diameter of 0.25 mm, chemically activated with a strong acid and then carbonized. The equilibrium adsorption isotherms were obtained using the batch method and then fitted to different adsorption models, such as the Langmuir or Freundlich models for liquid phase adsorption. The most significant adsorption parameters were optimized, such as the solution pH, mass of the adsorbent used, adsorption contact time and adsorption temperature. The kinetics of the sertraline adsorption on the adsorbent was estimated using the pseudo-first and pseudo-second order models. Obtained results in this work clearly show that olive stones, usually a residue from the Portuguese and Mediterranean oliviculture, can be exploited as a promising and low-cost bio-mass source on the production of adsorbent materials with considerable potential to remove micropollutants, such as the antidepressant sertraline, from water.

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Remediación y recuperación de fósforo con materiales nanoestructurados con potencial reaprovechamiento como fertilizantes

David Gómez-Carnota*, José L. Barriada, Roberto Herrero

Centro de Investigaciones Científicas Avanzadas, As Carballeiras s/n, A Coruña, España
Universidade da Coruña, Departamento de Química, Rúa da fraga 10, A Coruña, España
**e-mail del autor de contacto: david.gcarnota@udc.es*

En este trabajo se ha desarrollado un material de bajo coste con una superficie nanoestructurada, con capacidad de retención de hierro y fósforo y con posible reaprovechamiento directo como fertilizante de cultivo. Para ello, se sintetizó una base polimérica formada a partir de silicato de sodio (GSP), la cual se funcionalizó con hierro mediante adsorción [1]. El material resultante (GSP-Fe) se empleó para la recuperación de fósforo en forma de iones fosfato.

El hierro es el elemento que actúa como adsorbente, mientras que la base polimérica funciona única y exclusivamente como soporte del hierro y no interviene en la reacción. El hierro se adsorbe uniformemente sobre la superficie nanoestructurada de la base polimérica; de esta manera se consigue que el hierro funcione bien como adsorbente, evitando problemas como aglomeración de partículas o la dificultad de retirar el adsorbente tras la reacción.

Se estudiaron 3 tamaños de partícula, buscando una relación óptima entre eliminación y facilidad de manipulación. Se emplearon partículas de diámetro entre 0.5 y 1 mm (fracción S-1), partículas con diámetro entre 0.5 y 0.25 mm (S-0.5) y partículas de diámetro inferior a 0.25 mm (S-0.25). La caracterización del material se realizó mediante SEM, EDS, XPS, TGA y fisisorción de N_2.

Se analizaron las cinéticas de reacción empleando el modelo de difusión de Boyd [2], y los equilibrios de adsorción utilizando distintos modelos de isoterma de adsorción (Langmuir, Langmuir-Freundlich, Sellaoui et al. [3]). Los procesos de adsorción de hierro y fósforo, según el modelo de Boyd, son principalmente procesos de difusión cuya etapa limitante es la difusión film. Al estudiar los equilibrios se encontró una adsorción máxima de hierro sobre la base polimérica de 23,9 ± 0,3 mg Fe·g^{-1} GSP. Para la adsorción de fósforo el valor máximo es de 301 ± 9 mg P·g^{-1} Fe. Estos valores están asociados a la superficie y porosidad de cada una de las fracciones de los materiales.

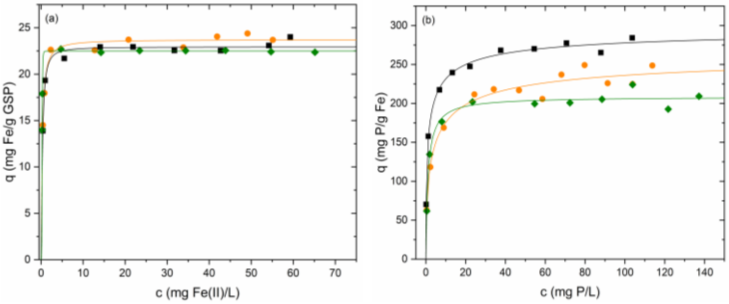

Fig.1. Equilibrios de adsorción de hierro y fósforo. ● Fracción S-1, ♦ fracción S-0.5, ■ fracción S-0.25.

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Geoquímica e biodisponibilidade do Cu em solos de manguezais da Baía de Todos os Santos, Bahia, Brasil

Mônica A. V. Ramos[1,*], Xosé Luis Otero Pérez[2]

[1]Universidade de Santiago de Compostela, Departamento de Edafologia e Química Agrícola, Santiago de Compostela, Espanha
[2]Universidade de Santiago de Compostela, Departamento de Edafologia e Química Agrícola, Santiago de Compostela, Espanha
monica_arlinda@yahoo.com.br

Os manguezais constituem ecossistemas costeiros sujeitos ao regime das marés, sendo ambientes de grande importância para a reprodução da fauna marinha e estuarina, para a proteção da faixa costeira contra eventos climáticos e para a estocagem de carbono. Apesar da sua importância, são ambientes ameaçados pela supressão e fragmentação dos seus bosques, pelas mudanças climáticas e pela contaminação química [1,2,3,4].

A Baía de Todos os Santos (BTS), segunda maior baía do Brasil, abriga em seu entorno extensas áreas de manguezal [5], muitos dos quais com histórico de contaminação química por metais e hidrocarbonetos. Compreender o comportamento geoquímico dos metais nesses ambientes é de grande importância para o entendimento da sua mobilidade e toxicidade. Deste modo, este estudo teve por finalidade investigar o comportamento geoquímico do Cu e sua biodisponibilidade em manguezais da BTS.

Amostras de solos foram coletadas e quatro manguezais (Cacha Prego, CP; Ponta Grossa, PG; Ilha de Maré, IM; e Pitinga, PT), na estação seca (DS) e chuvosa (WS). Os solos foram caracterizados quanto à textura, carbono orgânico total (COT%), nitrogênio total (N total), razão C/N, Fe total e frações, Cu total e frações. O grau de piritização do Fe (DOP%), do Cu (DTMP %) e o fator de enriquecimento (FE) foram calculados em cada área.

Variação espacial foi observada em relação aos teores de Cu e Fe, e aos atributos físico-químicos dos solos. O Cu em IM superou de 5 a 21 vezes as concentrações encontradas nas outras áreas, com fator de enriquecimento elevado, associado à fonte antrópica ou à atividade da biota. Neste manguezal foi encontrado o maior teor de grãos finos, assim como os maiores valores de COT (3,1 - 8,8%), de Fe total, e do DTMP-Cu (%), características que favorecem a retenção dos metais em condições redutoras [6,7,8].

A maior parte do cobre biodisponível foi encontrada associada à pirita e à matéria orgânica, exceto em Pitinga (DS), onde os maiores valores biodisponíveis foram associados aos óxidos de Fe cristalinos. Os elevados teores encontrados no solo de IM sugerem que a poluição por cobre constitui um estressor neste manguezal, com risco à qualidade deste ecossistema e à biota residente.

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Valorización de sub-productos de la industria agroalimentaria gallega a través de la Química Verde

M. Celeiro[1,2*], **A. Castillo**[1,2,3], **L. Rubio**[1,2], **C. Garcia-Jares**[1,2], **M. Lores**[1]

[1]LIDSA- Departamento de Química Analítica, Nutrición y Bromatología,
Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España
[2]CRETUS- Departamento de Química Analítica, Nutrición y Bromatología,
Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España
[3]I-Grape Laboratory, Avda Mestre Mateo, Ed. Emprendia, 15702, Santiago de Compostela, España
**maria.celeiro.montero@usc.es*

Se calcula que los viñedos ocupan una superficie de 3,000M de hectáreas en todo el mundo. Durante la producción de vino, aproximadamente el 25% del peso de uva se convierte en un residuo, llamado "bagazo". Su acumulación excesiva provoca un problema de gestión para las propias bodegas, debido a que se acumulan grandes cantidades de este residuo en un pequeño intervalo de tiempo, así como un problema medioambiental.

En los últimos años, la disponibilidad tecnologías de análisis modernas junto con los principios de la "Química Verde", permiten la reutilización efectiva de los subproductos agroalimentarios mediante la elaboración de productos de valor añadido. Debido a las características de la vinificación de los vinos blancos, el bagazo generado durante la vinificación es muy rico en polifenoles, conservando la mayor parte de la carga polifenólica original de la uva.

El objetivo principal de este trabajo es la obtención de extractos de bagazo de uva blanca (Albariño) ricos en compuestos bioactivos para elaborar productos naturales antimicrobianos y antioxidantes de alto valor. Para ello, se propone un procedimiento respetuoso con el medio ambiente basado en un sistema MSAT (medium-scale ambient temperature) [1]. Esta configuración permite fácilmente el escalado posterior hasta la producción preindustrial. El sistema MSAT cumple con los principios de la química analítica verde (GAC) ya que se emplean disolventes GRAS (generally recognized as safe) para modular el perfil de los compuestos bioactivos.

Los extractos obtenidos se caracterizaron en términos de contenido polifenólico total (IPT) y capacidad antioxidante (AA). También se empleó la cromatografía líquida acoplada a espectrometría de masas en tándem (LC-MS/MS) para cuantificar los compuestos fenólicos individuales. Los resultados revelaron la presencia de un elevado número de compuestos bioactivos de hasta cientos de mg L^{-1}. Los extractos también presentan una elevada actividad antimicrobiana frente a diferentes patógenos.

El objetivo último de este trabajo es emplear estos extractos como complementos y/o alternativas eficaces a los principales antibióticos utilizados en animales de granja mediante el uso de productos funcionales naturales más asequibles procedentes de fuentes alternativas.

Agradecimientos

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AMB17

Development of a Sustainable Recovery Process of Indium from Liquid Crystal Displays of Smartphones Waste

Liliana M. Martelo [1*], Márcia A. D. Silvia[1,2], Paulo M. S. Sousa[1], Margarida M. S. M. Bastos[2], Helena M.V.M. Soares[1]

[1] REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2] LEPABE/ALICE, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal
**e-mail: lmartelo@fe.up.pt*

Indium tin oxide (ITO) films used in liquid crystal displays (LCD) screens in smartphones account for nearly 80% of the total consumption of indium (In) worldwide and is one of the critical raw materials (CRMs) in the 2020 List of CRMs for the EU. An LCD screen is a sandwich structure composed of two glass substrates covered with the ITO glass within the liquid crystals between the glass and the polymeric film [1]. The current implemented recycling process usually adopts mechanical crushing or pyrolysis [2-3] as the primary step for the treatment of LCD screens. However, the toxic materials (liquid crystals) and valuable recyclable materials (In) are treated together and the recovery rate of In is considerably low. Although the amount of In available in LCD screens is about 102 mg/kg, it can increase up to 1400 mg/kg per screen [3], if the polymeric film attached to the LCD screen is previously removed. An effective liberation and size-reduction method of ITO glass is an important pre-treatment step that involves removing the polymeric film and dissolution of liquid crystals, aiming to obtain the ITO-glass as raw material for subsequent selective recycling of In.

To address this issue, here we propose a hybrid (chemical plus physical steps) method, that removes the polymeric film attached to the ITO glass to recover the highest amount of In and dissolve the liquid crystals using a mixture of water and ethyl acetate (1:5) in a sealed low-pressure reactor (1 hour at 180 ºC) (**Fig. 1**). Subsequently, the recovery of In from the ITO glass was performed under soft acid leaching conditions assisted by microwave (0.25 M of HCl, solid/liquid ratio: 1/10, 2 cycles of 2 minutes), with a high recovery yield of In (99.0%) followed by continuous column ion-exchange technology (IET) to purify In from other impurities (mainly tin, aluminum and copper). All these improvements resulted in a simple and feasible flowsheet, which can be, later on, scaled-up and be easily used in the industry.

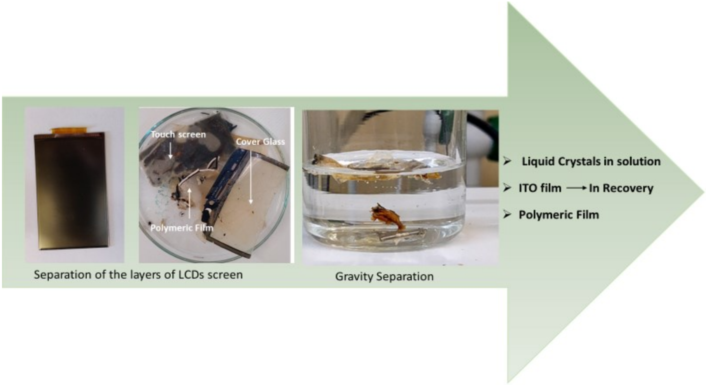

Fig.1. Flowsheet of the proposed method to recover indium from the LCDs wastes of smartphones.

Acknowledgments:

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Iron determination in natural waters using a synthesized 3-hydroxy-4-pyridione ligand in a newly developed µfluidic paper-based device

Juliana I. S. Aguiar[1*], Susana O. Ribeiro[2], Andreia Leite[2], Maria Rangel[3], António O. S. S. Rangel[1], Raquel B. R. Mesquita[1]

[1]Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 137, 4169-005, Porto, Portugal
[2]Universidade do Porto, Faculdade de Ciências, Departamento de Química e Bioquímica, REQUIMTE-LAQV, 4169-007, Porto, Portugal
[3]Universidade do Porto, Instituto de Ciências Biomédicas de Abel Salazar, REQUIMTE-LAQV, 4050-313, Porto, Portugal
*jiaguiar@ucp.pt

The assessment of the global water quality has been the subject of intense research, namely the heavy metal pollution of water. At specific amounts, iron is essential to different organisms for their proper growth and is one of the several heavy metals found in water sources. When in excess, iron produces negative effects in the environment, damaging aquatic ecosystems. The presence of iron in waters can result from geogenic sources or via dumping of domestic waste and industrial effluents, namely iron and steel industries, mining and metal corrosion. In this context, the amount of iron in natural waters can be a powerful indicator of its quality.

In this work, a microfluidic paper-based analytical device (µPAD) was developed to determine iron concentration in all types of natural waters, for *in situ*, real time analysis. The determination was based on the colorimetric reaction of iron with a new 3-hydroxy-4-pyridione ligand, as a colour reagent. The design of the µPAD and the operational parameters were studied and, under the optimized conditions, a linear calibration curve in the concentration range of 0.25 – 2.00 mg/L was obtained, with a limit of detection of 0.07 mg/L. After validation, the proposed µPAD was successfully applied to the determination of iron in several types of water (with no need of sample pre-treatment): tap, well, river and sea waters and proved to be an effective, low-cost, sensitive method for a simple implementation to carry out *in situ* analysis.

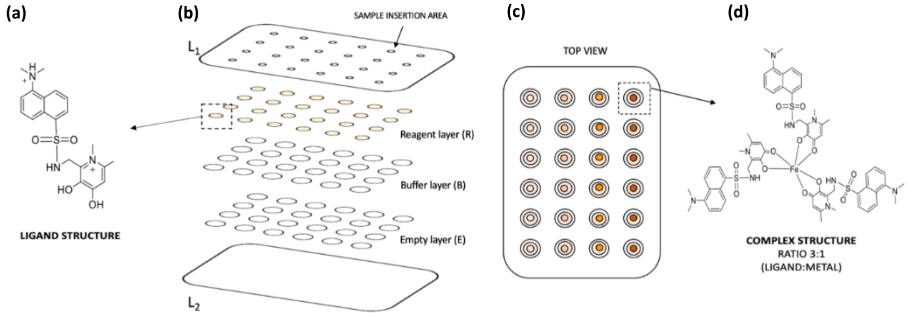

Fig.1. Schematic representation of the µPAD for iron determination: (a) ligand structure; (b) alignment of the paper discs into layers; (c) top view after loading the iron standards; (d) iron complex structure.

Acknowledgments
A. Leite and R.B.R. Mesquita thank FCT/MCTES (Fundação para a Ciência e Tecnologia and Ministério da Ciência) for funding through program DL 57/2016 – Norma transitória. This work received financial support from National Funds FCT/MCTES, under the Partnership Agreement PT2020 through project PTDC/QUI-QIN/28142/2017. Additionally, the research team would like to thank FCT the projects NORTE-07-0162-FEDER-000048 and UIDB/50016/2020.

AMB19

Pre-treatment to increase gold recovery from integrated circuits of smartphones wastes

Márcia A.D. Silva[1,2*], Liliana M. Martelo [1,] Margarida M.S.M. Bastos[2], Helena M.V.M.Soares [1]

[1] REQUIMTE/ LAQV, Departamento de Engenharia Química, Faculdade Engenharia Universidade do Porto
[2] LEPABE - Departamento de Engenharia Química, Faculdade Engenharia Universidade do Porto
e-mail: up201502999@fe.up.pt

Integrated circuits (ICs) are the major electric components of printed circuit boards. ICs perform many functions, such as amplifier, oscillator, timer, counter, logic gate, computer memory, micro-controller, or microprocessor. ICs are mainly constituted by silicon dioxide reinforced with brominated epoxy resin (BER) (to support high temperatures) and a metallic fraction constituted by around 7 kg of Ag, 5 kg of Au, 110 g of Pd and 4 g Pt per ton of IC along with Cu (35,68 kg/ton IC), Pb (55,89 kg/ton IC), Fe (15,29 kg/ton IC) and Ni (5,56 kg/ton) [1], [2].

The non-metallic fraction of ICs is harder to break or dissolve without environmental damage. Up to now, vacuum pyrolysis, roasting and grinding are the most used processes to recycle the metallic fraction of ICs but these processes have several disadvantages at an environmental point of view, such as, the emission of toxic gases and high energy consumption. Furthermore, a relevant loss of precious metals, such as, gold is reported [3].

Here, we propose a different approach, based on a combined physical process, that allows to separate a fraction enriched in precious metals (namely, gold) from other fraction mainly constituted by base-metals (mostly iron, nickel and copper) turning the recovery yield of precious metals higher. The developed process consists on pressing the ICs sample at 400 bars, followed by sieving for separation into three size ranges (to remove the epoxy resin) and, then, a separation based on their differences of magnetic properties was performed at the end. The sequence of these physical processes allowed to concentrate more than 80% of the gold (1.46 Au mg/g non-magnetic fraction) in the non-magnetic fraction with a low percentage of other based metals as contaminants.

The implementation of this physical process allows to pre-concentrate the amount of gold on the precious metals enriched fraction for its subsequent recovery using a chemical process, which is of paramount importance since it will allow to reduce drastically the amount of reagents needed for leaching and, thus, turns the overall process more environmentally sustainable.

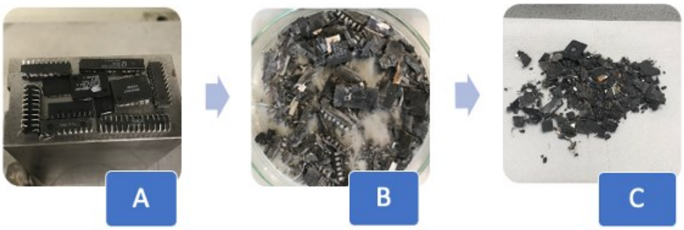

Fig.1. A- Initial sample of several ICs, B- ICs after being crushed twice with 400 bars using a hydraulic press, C- The non-magnetic fraction containing 80% of the Au present in the initial sample after sieving process.

Acknowledgments

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Valorization of vine shoots to extract lignin – chemical and structural characterization

Ana Rita Pereira*[1], **Carina Costa[2*]**, **Victor de Freitas[1]**, **Nuno Mateus[1]**, **Alírio Rodrigues[2]**, **Joana Oliveira[1*]**

[1] Laboratório Associado para a Química Verde - REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
[2] LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; ALiCE - Associate Laboratory in Chemical Engineering, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal;
* anarita@fc.up.pt; * caecosta@fe.up.pt; * jsoliveira@fc.up.pt

One of the most significant food sectors in the world is the wine industry. Portugal is ranked as the world's eleventh-largest wine producer by the International Organization of Vine and Wine [1]. As a result, millions of tons of organic waste are created every year, particularly vine pruning material. These residues are burned or used as a domestic fuel in agricultural fields because of their calorific value; however, release greenhouse gases and heat the atmosphere [2]. The vine pruning material corresponds to 93% of the residues generated, and it is important lignocellulosic biomass containing cellulose (32.9-39.9%), hemicellulose (5.8-27%), and lignin (26.7-46.8%) [3]. This work proposes the reuse of this material as a feedstock to extract lignin by mild acidolysis to avoid extensive structural lignin changes (Figure 1). Several pre-treatment conditions of plant material and the influence of the purification process were evaluated. Different lignin fractions (AM1, AM2, AM3, and AM4) were structurally characterized through ^{13}C NMR, Gel permeation chromatography and Fourier transform infrared spectroscopy. Structural analysis of the different lignin fractions suggests a similar composition independent of the extraction and the purification methods, with β-O-4 structures content around 60 per 100 aryl units and Syringyl/Guaiacyl (S/G) ratio about 1.50. The main change was the increase of the degree of the condensation (DC) ranging from 9 to 21% for pre-treatment with ethanol/toluene and water/toluene, respectively. It is described in the literature that this feedstock has a significant content in tannins [4]. Dioxane lignin extracted with ethanol/toluene showed a higher value of condensed tannins around 11%; however, the results proved that the dialyzes method helps to purify the sample with special attention for the decrease of proanthocyanidins content (around 3% for sample pre-treated with ethanol/water followed by dialyzes). The obtained dioxane lignin can be further used as a biopolymer to produce nanoparticles for the color stabilization of different dyes.

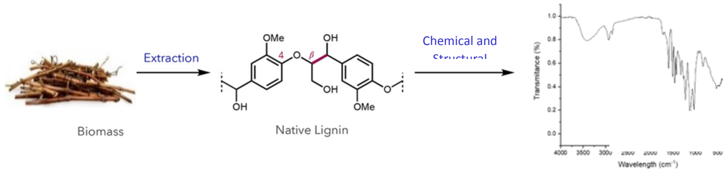

Fig.1. Isolation of lignin by mild acidolysis process and subsequent chemical and structural characterization

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Bioacumulação de Cu em tecidos de *Ucides cordatus* em manguezais da Baía de Todos os Santos, Bahia, Brasil

<u>Mônica A. V. Ramos[1]</u>, Xosé Luis Otero[2]

[1]Universidade de Santiago de Compostela, Departamento de Edafologia e Química Agrícola, Santiago de Compostela, Espanha
[2]Universidade de Santiago de Compostela, Departamento de Edafologia e Química Agrícola, Santiago de Compostela, Espanha
monica_arlinda@yahoo.com.br

A contaminação química por metais constitui uma ameaça aos ecossistemas, incluindo os ambientes costeiros, com riscos associados à biota e à saúde humana, uma vez que podem ser bioacumulados pelos organismos e transferidos via cadeia trófica, com possibilidade de biomagnificação [1].

A baía de Todos os Santos, segunda maior baía do Brasil, abriga extensas áreas de manguezal e zonas de pesca e mariscagem. Apesar da sua importância, é uma área vulnerável à contaminação química, principalmente nas regiões norte e nordeste [2], onde se concentram diversos empreendimentos, incluindo refinarias de petróleo, portos e terminais marítimos. Diante da vulnerabilidade deste ecossistema, este estudo teve por finalidade determinar os teores de Cu assimilados pelo *Ucides cordatus* em manguezais da Baía de Todos os Santos, bem como avaliar os riscos associados ao consumo deste crustáceo pela população humana.

Amostras de U. cordatus foram coletadas em quatro manguezais (Cacha Prego, CP; Ponta Grossa, PG; Ilha de Maré, IM; e Pitinga, PT), na estação seca (DS) e chuvosa (WS). Os espécimes foram dissecados para retirada do tecido branquial, hepatopâncreas e músculo, a partir dos quais foram constituídas amostras compostas. Para a determinação do analito, as amostras foram liofilizadas durante 72h, moídas e digeridas em bloco digestor com 7 ml de HNO3 e 2 ml de H2O2 de qualidade ultrapura. O material digerido foi avolumado para 25 ml com água Mili-Q e as concentrações foram analisadas por Espectrometria de Absorção Atômica (Perkin Elmer). O método analítico empregado foi validado por meio de material de referência certificado de amostra animal (NIST - 1577b, bovino liver), com taxa de recuperação superior a 90%.

Os teores de Cu variaram entre 20,24 µg.g-1 e 1320 µg.g-1, com os maiores valores no hepatopâcreas e nas brânquias. As concentrações no músculo e no tecido branquial foram mais elevadas nos crustáceos coletados em Ilha de Maré, enquanto no hepatopâncreas valores elevados foram encontrados tanto em Ilha de Maré como em Pitinga, sem diferença entre essas áreas ($p>0,05$).

As concentrações de Cu verificadas em PT e IM foram superiores aos resultados até então publicados para *U. cordatus* no Brasil [3,4,5,6] e estão acima dos limites permitidos pela legislação brasileira (Decreto nº55.871de 1965) e internacional [7].

Agradecimentos
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Geopolímeros desde residuos de tierras diatomeas para el tratamiento de aguas residuales de la industria vitivinícola

Y. Huaccallo-Aguilar[1,2]*, **Jose L. Diaz de Tuesta**[1], **A. P. Silva**[1,2], **Oscar Lima**[3], **H. T. Gomes**[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3] Caves Campelo, S. A., Rua Joaquim Miranda Campelo 586, 4755-326 Moure, Portugal.

* *ysabel@ipb.pt*

A nivel mundial, los residuos industriales están incrementando. Las tierras diatomeas después de ser utilizadas en la industria vitivinícola son destinadas a los rellenos sanitarios. Sin embargo, estos residuos pueden utilizarse para la preparación de filtros para el tratamiento de aguas residuales [1,2]. En este sentido, nuestra investigación se enfocó en la síntesis y aplicación de geopolímeros a partir de tierra de diatomeas usadas (TD) con/sin la incorporación de carbón activado comercial (AC) para el tratamiento de aguas residuales de la industria vitivinícola (ARIV). Así, en este trabajo se informa de un método para la síntesis de geopolímeros con diferentes composiciones (cinco fórmulas), y su caracterización mediante el método de espectroscopia infrarroja por transformada de Fourier (FT-IR) y el análisis de las isotermas de adsorción-desorción de nitrógeno a 77 K [3]. La aplicación de estos geopolímeros de TD se probaron en la adsorción de carbono orgánico total (COT), nitrógeno total (NT) y compuestos aromáticos (ARO) de ARIV en modo estático. Previo al tratamiento con los geopolimeros, el ARIV se caracterizó con un alto carbono orgánico total inicial (54 123 g L^{-1}) y un pH inicial bajo (3,6). Desde de la aplicación, el geopolímero TD/AC que contiene 3,5% de AC (sF1-3.5A) reveló una eliminación de carbono orgánico total (COT) de hasta el 52% tras 6 h. La segunda eliminación de COT más elevada (42%) se obtuvo con el geopolímero sF1 (Tabla 1). Respecto a los ensayos de blanco con sólo TD o sólo carbón activado (equivalente a la cantidad utilizada en sF1-3.5A), la eliminación de COT fue del 5% y del 14%, respectivamente, poniendo así en evidencia el sinergismo obtenido con el geopolímero desde TD y el carbón activado. En conclusión, las tierras diatomeas desgastadas son residuos sólidos que pueden aprovecharse como precursores para la preparación de geopolímeros. Los geopolimeros híbridos demostraron ser una alternativa para los tratamientos de aguas residuales de la industria vitivinícola.

Tabla 1. Eficiencia de eliminación de parámetros seleccionados de las aguas residuales industriales

Nº	NaOH (mol)	Na_2SiO_3 (mol)	TD (g)	Al_2O_3 (mol)	AC (g)	Eliminación de COT (%)	Eliminación de NT (%)	Eliminación de ARO (%)
sF1-3.5A	0,004	0,088	23,7	0,047	0	53,11	52,13	56,99
sF3-1.2A	0,100	0,021	23,7	0,047	0	41,82	31,51	37,20
sF1	0,100	0,021	23,7	0,031	0	48,25	42,12	39,10
sF3	0,100	0,021	23,7	0,047	0,4	32,79	30,60	11,14
sF5	0,004	0,088	23,7	0,047	1,5	47,16	31,68	20,62

Condiciones experimentales: COT_0 = 54123 mg L^{-1}, temperatura = 20 ºC, masa de geopolímeros = 2,2 g; tiempo de contacto = 6 h, y pH = 4,6.

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Potential of macroalgae to remove rare earth elements from contaminated waters

<u>Eduarda Pereira</u>[1,2*], João Pinto[1], Filipe L.S. Monteiro[1], Jéssica Jacinto[1], Daniela S. Tavares, Nicole Ferreira, Thainara Viana, João Colónia, Bruno Henriques[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[2]LCA, Department of Chemistry, University of Aveiro, Aveiro, Portugal
**eduper@ua.pt*

The European Union has classified rare earth elements (REE) as critical raw materials of high economic value and commercial interest, with a wide range of applications. Their criticality results from the difficulty and high costs associated with their exploration as well as from geopolitical supply bottlenecks [1]. Therefore, to promote a sustainable exploration of these resources, the recovery of these elements from secondary sources is highly recommended. The present work represents one of such efforts, in which a sorption-based technology using different living macroalgae was used to remove and concentrate REE from waters contaminated by e-waste leachates. The potential of live macroalgae as REE sorbents was evaluated by kinetic tests in mono- and multi-contaminated solutions, involving the REE Cerium (Ce), Europium (Eu), Yttrium (Y), Lanthanum (La) and Neodymium (Nd) from saline water, with an initial concentration of 500 µg L^{-1}, to which was added approximately 500 mg L^{-1} in dry weight of live macroalgae *Gracilaria gracilis*, *Fucus vesiculosus* and *Ulva lactuca*. Element quantification was performed by ICP-OES.

While all macroalgae showed removal efficiencies > 40 %, the removal rates achieved by the red seaweed *G. gracilis* stood out, with values between 60 and 99 % for the studied REE (**Fig. 1**). The multi-contaminated solutions showed higher removal efficiencies than those from mono-contamination, further proving the absence of selectivity for the different REE tested. Kinetic studies showed that equilibrium was not reached in 48 h, implying that the removal of REE could potentially be higher at optimal exposure times. The quantification of REE in the biomass was in line with the mass balance expectations, proving the potential of macroalgae for the removal, concentration and recovery of REE from e-waste contaminated water as a simple, economical and environmentally friendly process.

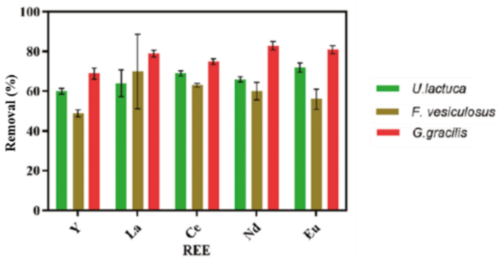

Fig.1. Removal (%; mean) of REE from e-waste contaminated water (standard deviations are represented by the error bars), after 48 h of contact with the macroalgae *U. Lactuca*, *F. vesiculosus* and *G. gracilis*.

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Glyphosate and Aminomethylphosphonic acid adsorption in soils

Maria J. Fernandes[1,2*], Paula Paíga[1], Sónia Figueiredo[1], Felipe Macías[2] & Cristina Delerue-Matos[1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, Porto, Portugal;
[2] IIT/LTA- Instituto de Investigaciones Tecnologicas, Universidad de Santiago de Compostela, Santiago de Compostela, Spain
*mea@isep.ipp.pt

Glyphosate (GLY) is one of the most widely used herbicides in the world, representing 33% of the total herbicide sales in the EU28^{+3} (EU28+Norway, Switzerland, and Turkey) in 2017, meaning about 69% of the herbicides sold in Portugal and 23% in Spain. It is applied for agronomic purposes, including urban and agricultural weed control, crop desiccation, ending cover crops or grassland and renewing permanent grassland. Its widespread use is due to several characteristics as high efficacy, broad spectrum, and low cost, combined with the introduction of genetically engineered glyphosate-tolerant crops [1]. Aminomethylphosphonic acid (AMPA) is its primary metabolite and was found to be 3 to 6 times more resistant than GLY against degradation, which brings a higher concern to the environment safety [2]. GLY was considered safe for many years and with a good ecotoxicological profile. However, concerns about its toxicity and potential carcinogenicity have recently been raised. Its possible carcinogenicity triggered a strong public and political discussion. Different studies and institution assessments obtained contradictory results and thus led to controversial conclusions [3].

The presence of GLY and AMPA in soils, water/ground water [3], and air [4] are, already, well documented. Additionally, it was also found in human urine [5], revealing the exposure to which humans and animals are subjected. In 2009, EPA national primary drinking water regulations already presented GLY in the list of organic contaminants in drinking water, with a maximum concentration of 700 mg/L[6].

The GLY persistence in soils varies extensively, depending on temperature, soil moisture, type, binding extent, microbial breakdown, and phosphate levels, with a half-life ranging between 1 and 197 days. AMPA, which is more persistent in soil and water, presents a half-life ranging between 23 and 958 days [7]. The study of the soil adsorption of these compounds is essential to the development of methodologies for the remediation of contaminated soils.

The adsorption of GLY and AMPA was studied in eight soils with different characteristics concerning Fe, Al, Ca, Mg, Na, P, and K content, pH, pH at the point of zero charge, electrical conductivity (EC), organic matter (OM) and ions concentration (Cl^-, F^-, SO_4^{2-}, PO_4^3, NO_2^-, NO_3^-, NH_4^+). Preliminary adsorption experiments allowed the selection of the four soils with higher affinity to these contaminants. Batch and equilibrium experiments were performed, and the influence of pH was evaluated. The equilibrium was reached in approximately 14 hours in all systems. The maximum adsorption capacity obtained was 18,7 mg/g for GLY and 12,3 mg/g for AMPA, both for the same soil, characterized by a low pH (4,85), and a high OM content (23,4 %).

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AMB25

Searching for a new generation of environmentally compatible antifouling agents

Cátia Vilas-Boas[1,2], Ana Rita Neves[1,2], Diana Resende[1,2], Elisabete R. Silva[3], Madalena Pinto[1,2], Emilia Sousa[1,2], Elizabeth Tiritan[1,2,4], Joana R. Almeida[2], Marta Correia-da-Silva[1,2*]

[1]FFUP - Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal; [2]CIIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Matosinhos, Portugal; [3]BioISI - BioSystems & Integrative Sciences Institute, Faculty of Sciences, University of Lisbon, Portugal; [4]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, CESPU, CRL, Gandra, Portugal;
*m_correiadasilva@ff.up.pt; dedicated by the author to the memory of Professor Costa Lima

The addition of biocides to marine coatings has been the most used solution to avoid marine biofouling, however they were found to be persistent, bioaccumulative, and toxic (PBT) to marine ecosystems. The development of lab-synthesized compounds inspired in natural metabolites to supply the high market demand and replace these harmful biocides has been pursued in the last years as one of the most promising and eco-friendly antifouling (AF) solutions.

Following a bioprospection strategy, our group has previously reported the AF activity of gallic acid persulfate (**1a**) and 3,4-dioxygenated xanthone (**2a**), two nature-inspired compounds, against the settlement of *Mytilus galloprovincialis larvae* (EC_{50}= 18 and 11.53 µM, respectively) without exhibiting ecotoxicity to *Artemia salina* (<10% of mortality) [1, 2]. In order to improve potency while maintaining a low ecotoxicity profile, a lead optimization strategy was applied to compound **1** and **2**. From two series of derivatives, it was possible to obtain 2-(3,4,5-trihydroxybenzamido)ethan-1-aminium bromide (**1b**,) and C-1 aminated 3,4-dioxygenated xanthone (derivative **2b**) (EC_{50}= 3 and 7.28 µM, respectively), with 1**b** being more potent than the emergent biocide Econea® (EC_{50}= 4 µM) [2, 3].

The environmental impact of these two optimized compounds was studied namely regarding ecotoxicity, bioaccumulation potential, abiotic degradation, and bioaccumulation potential, leaching to seawater and bioactivity after incorporation in coatings [1, 4] (Table 1). The four synthesized compounds presented low bioaccumulation potential (Log Kow < 3.5). Concerning abiotic degradation (DT_{50}), compound **1a** and Econea® were classified as persistent in abiotic seawater, whereas derivative 1**b** presented a DT_{50} lower than 24 hours. All compounds maintained their AF properties after being incorporated into coatings, with derivatives **1b** and **2b** exhibiting the greatest anti-settlement effect. The leaching of compound **1b** from coatings was lower than that of compound **1a**. Compound **2a** and its derivative **2b** leached similarly. The overall properties of compound **1b** and **2a** favor their further studies *in situ*. This proof-of-concept helped to establish these new synthetic derivatives as promising efficient and eco-friendly AF agents.

Tabla 1. Environmental fate and AF effectiveness assessment in coatings [1-3].

Compound	Abiotic degradation (DT_{50})	Bioaccumulation potential (Log Kow)$^{\#}$	Anti-settlement effect after coating incorporation (%)	Leaching (wt.%)
1a	> 60 days (persistent)	-7.02	0^{a}	18.5^{a}
1b	< 24 hours	-0.79	63.6^{a}	8.79^{a}
2a	32-51 days	2.88	54.5^{a}	0.003^{a}
2b	49-59 days	3.49	100^{b}	1.69^{b}
Econea®	> 60 days (persistent)	4.69	9.1	1.57

$^{\#}$Evaluated in silico though EPI Suit; ^{a}Polyurethane (PU) marine coating; ^{b}room-temperature-vulcanizing polydimethylsiloxane (RTV-PDMS) coating.

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AMB26

Screening of the main factors affecting the microwave-assisted extraction (MAE) of phenolic compounds from cork industry waste

Azevedo, J.[1,*], Cassani, L.[2,3], Oliveira, J.[1], Chamorro, F. [2], Perez-Gregorio, R.[1,2], Simal-Gandara, J. [2],Lopes, P.[4], Mateus, N.[1], Freitas, V.[1] and Prieto, M. A.[2,3]

[1] LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
[2] Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.
[3] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[4] Amorim Cork, Rua dos Corticeiros, Mozelos, Portugal
*joana.azevedo@fc.up.pt

The recovery of added value bioactive compounds from industrial food wastes contributes to sustainability and to upcycling solutions [1]. Among green extraction techniques, microwave-assisted extraction (MAE) stands out since the heat and mass transfers are in the same direction, likely to result in a synergistic effect that increases extraction rate and yield. Furthermore, MAE application provides reduced thermal degradation and use of organic solvents, and selective heating of vegetal material [2]. Thus, the main objective of this work was to study the impact of different factors (time, power, and solvent concentration (% ethanol)) involved in the MAE of phenolic compounds from cork industry waste. To this aim, a factorial design was applied considering the time (45 s-4.5 min), power (300-700 W), and solvent concentration (10-90% ethanol). Extraction yield (EY) and total phenolic content (TPC) were the response variables in the factorial regression. EY was gravimetrically determined and TPC was calculated as the sum of all phenolic compounds individually identified by LC-MS/MS for each of the eight runs. Results revealed that time, power, and solvent concentration had a significant effect on extraction yield ($p<0.001$), suggesting that the higher the values of factors, the higher the extraction yield was 83.52 mg extract/ g dw (Run 7, **Table 1**). Concerning TPC, it was possible to obtain in best conditions 1.81 mg/g dw of TPC with gallic acid, vanillin, and the isomers castalagin and vescalagin as the main compounds obtained.

Table 1. Factorial design for the study of factors influencing the phenolics extraction from cork industry waste using MAE.

		Factors			**Response variables**	
Run order	**Standard order**	**Time (min)**	**Power (W)**	**Solvent concentration (% ethanol)**	**Extraction yield (mg extract/ g dw)**	**Total phenolics content (mg/ g dw)**
1	4	4.5	700	10	51.30	1.53
2	5	0.75	300	90	26.14	0.27
3	3	0.75	700	10	15.96	0.37
4	6	4.5	300	90	56.85	0.55
5	7	0.75	700	90	51.38	0.55
6	1	0.75	300	10	17.74	0.55
7	8	4.5	700	90	83.52	1.81
8	2	4.5	300	10	25.28	0.93

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Comparison of Advanced Tertiary Treatments for Pharmaceuticals Removal from a Municipal Wastewater

***E.Surra*[1,*]*, C.Ribeiro*[1]*, P.Paíga*[1]*, I.Baptista*[2] *, L.Marinheiro*[3]*, N.Lapa*[4]*, C.Delerue-Matos*[1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Instituto Politécnico do Porto, Porto, Portugal
[2]WEDOTECH, Lda., Rua do Seixal, 108, 4000-521 Porto, Portugal
[3]AST – Soluções e Serviços de Ambiente, Lda., Rua do Bairro, 400, 4485-010 Aveleda, Portugal
[4] REQUIMTE/LAQV, Dep. Química, NOVA School of Science and Technology, NOVA University Lisbon, Caparica, Portugal
**elena.surra@graq.isep.ipp.pt*

Pharmaceuticals (Ph) have been detected usually at concentrations between ng/L to µg/L in Municipal Wastewaters (MWW) representing a continuous source of contamination to the environment [1]. The presence of these Ph raises environmental concerns due to their bioaccumulation potential, endocrine-disrupting effects, and inhibition potential of photosynthesis and plant growth.

This work compares the environmental sustainability along with Ph removal efficiency of three different advanced tertiary treatments, namely sand filter (SF) coupled with ozonation (OZ), ultrafiltration (UF), and UF coupled with nanofiltration (NF), with the tertiary treatment SF coupled with ultraviolet disinfection (UV), which already exists at the Portuguese Waste Water Treatment Plant taken as reference. The comparison of the treatment configurations was developed by applying the Life Cycle Analysis approach, using OpenLCA1.11 Software equipped with Ecoinvent 3.5 database, according to USEtox (recommended + interim) method, which was added with some of the missing characterization factors (CF) for Ph.

The results obtained showed that the tertiary treatments, which provided the highest Ph removal efficiency are SF+OZ and UF+NF, being UF+NF slightly more efficient for most of the Ph detected. Among them, SF+OZ showed better environmental performance than UF+NF in the impact category of Freshwater toxicity and Human cancerogenic and non-cancerogenic toxicity with values of 8.16E+03 PAF.m^3.day, 1.59E-07 cases and 1.44E-07 cases, respectively, on average 84% lower than the corresponding values obtained for UF+NF. This is due to the highest electric energy consumption, the use of the reagents as citric acid and sodium hypochlorite for the chemical wash of the membranes, and the indirect impacts associated with UF and NF construction. The impacts obtained for SF+OZ are based on operational data measured at the pilot scale within the scope of the present work. They are associated with an electric energy consumption higher than that recorded at commercial ozone units, and lacks of the indirect impacts associated to the market of liquid oxygen, which has to be accounted for most of the full scale units. It is expectable that, at commercial scale, the environmental advantages of SF+OZ can suffer some changes.

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Low-cost natural biosorbents for the treatment of contaminated waters

Paula Figueira[1,2*], **Bruno Henriques**[1], **Carlos Vale**[2], **Eduarda Pereira**[1]

[1]LAQV-REQUIMTE & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CIIMAR, University of Porto, 4450-208 Matosinhos, Portugal
**paulafigueira@ua.pt*

Contamination of water bodies by toxic elements from discharged untreated effluents has been a worldwide major environmental issue. Elements such as arsenic, lead, mercury, cadmium, chromium, cobalt, nickel and zinc are present in various effluents due to their vast use in numerous industrial processes. Since these elements can cause adverse effects on the environment and potential health damages in humans, even at low concentrations, their occurrence in waters has been increasingly restricted [1,2]. Thus, the development of innovative cheaper and cost-effective water treatment technologies is encouraged [1]. Additionally, it is important to adopt a water recycling and reuse approach to reduce the overexploitation of this natural resource, as the possible reuse of treated contaminated waters can be a sustainable way to protect drinking water supplies [3].

Biosorption, using unexpensive and commonly available materials has been shown as a promising alternative to traditional methods of water treatment such as chemical precipitation, coagulation/flocculation, membrane filtration or electrochemical treatments, since these methods can be expensive and often fail when the target is to reach very low residual levels or to treat large volumes of water [4]. Within biosorption, the use of agricultural wastes, such as nut shells, can be very attractive due to their low-cost and no commercial value together with their high content of lignocellulosic compounds, making them a viable option in the field of water treatment [5]. Although several works using nut shells as sorbents have been reported, most of them propose surface modifications and thermal treatments to improve the sorption capacity, but these procedures are time consuming and can be very expensive. Furthermore, most of the studies deal with the removal of a single contaminant and at unrealistically high concentrations, using large amounts of sorbents. In addition, few studies can be found testing solutions more complex than ultrapure water, which all together has delayed the transition of technology from laboratory to end-users.

This work assessed the capacity of unmodified hazelnut shells for the simultaneous removal of As, Cd, Co, Cr, Hg, Ni, Pb and Zn from contaminated mineral waters while identifying the best operational conditions for removal using the Response Surface Methodology combined with a Box-Behnken design. The optimization of experimental variables such as sorbent dose, pH, and initial element concentration was assessed for a maximum removal efficiency. Hazelnut shells proved to be an efficient sorbent for those elements (except for As), achieving removals between 76% and 96% under the optimum experimental conditions. The results evidence the feasibility of a low-cost sorbent for the removal of multiple elements under realistic environmental conditions (multi-contaminant systems, relevant concentrations of contaminants, low doses of sorbents and natural waters), to yield a cleaner water with potential reuse for further purposes, with lower water quality requirements than drinking water, such as agricultural irrigation, recreational uses or industrial applications.

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AMB29

Silver nanoparticles bioaccumulation assay in marine organisms

López-Mayán J.J.[*]**, Álvarez-Fernández B., Peña-Vázquez E., Barciela-Alonso M.C., Moreda-Piñeiro A., and Bermejo Barrera P.**

Trace element, Spectroscopy and Speciation group (GETEE), Instituto de materiais (iMATUS), Faculty of Chemistry, University of Santiago de Compostela, Av. das Ciencias s/n, 15782, Santiago de Compostela, Spain
**juanjoselopez.mayan@usc.es*

Silver nanoparticles (AgNPs) are one of the most widely used nanomaterials in the industry due to their bactericidal, antifungal and anticancer properties. These properties make them be used in several fields of application, including water and air purification, textile, electronics, medicine, drug delivery, dentistry, and use in personal care products, among others. Due to their extensive use, they are being released into the environment where they can be transformed by changing their size and shape, dissolve, or even react and interact with living beings. In addition, some studies indicate the possible toxicity of dissolved silver and AgNPs in plants, microalgae and vertebrates. Thus AgNPs can be considered as possible emerging contaminants.

The Nanoculture project consists of the administration of PVP-AgNPs to aquaculture products (mussels, turbot and algae). The main objectives of these bioaccumulation studies are to advance the knowledge, risk assessment and evaluation of their environmental presence. PVP-AgNPs bioaccumulation studies in red seaweed (*Palmaria palmata*), green seaweed (*Ulva sp.*) and mussels lasted 28 days with exposure doses of 0.1 and 1. 0 mg L^{-1} PVP-AgNPs. However, the bioaccumulation assay in turbot lasted 90 days with exposure doses of 0, 0.25, 0.75 and 1.5 mg of PVP-AgNPs per kilogram of fish and day.

Total Ag determination was carried out with inductively coupled plasma-mass spectrometry (ICP-MS) after microwave-assisted acid digestion in the three species. The Ag nanoparticle's content as well as their sizes were determined using the single particle-ICP-MS (SP-ICP-MS) and enzymatic extractions [1-2] that did not change the conformation and the size of the nanoparticles.

In the case of mussel, a total silver concentration and AgNPs concentration of 1.20±0.07 µg g^{-1} and $2.41\times10^{8}\pm4.49\times10^{7}$ part g^{-1} (at 28 days and 1.0 mg L^{-1} of PVP-AgNPs exposure dose), respectively, were reached. On the other hand, in the case of red seaweed, the maximum concentration of total Ag found was 0.79±0.06 µg g^{-1} (at 14 days and 1.0 mg L^{-1} of PVP-AgNPs dose), and the concentration of nanoparticles was $2.11\times10^{9}\pm6.83\times10^{8}$ part g^{-1} (at 28 days and 1.0 mg L^{-1} of exposure dose). In the case of green seaweed, the highest accumulation of total Ag was 0.46±0.15 µg g^{-1} (at 21 days and 1.0 mg L^{-1} of exposure dose), and the highest concentration of nanoparticles was $3.21\times10^{9}\pm3.99\times10^{8}$ part g^{-1} (28 days and a 1.0 mg L^{-1} of exposure dose). In the case of turbot, no bioaccumulation of total silver or AgNPs has been observed in any of the fish tissues studied.

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Removal of anthropogenic pollution markers with a nitrogen-doped reduced graphene oxide-PVDF membrane

Joaquín A. Marrero[1,2,*], Sara Ribeirinho-Soares[1,2], Rui S. Ribeiro[2,3], Adrián M. T. Silva[2,3], Olga C. Nunes[1,2]

[1]*Laboratory for Process and Reaction Engineering, Environment, Biotechnology and Energy (LEPABE), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[2]*Associate Laboratory in Chemical Engineering /ALiCE), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[3]*Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
** jmarrero@fe.up.pt*

This work presents, for the first time, the efficiency of a continuous flow mode system for water disinfection recruiting the functionalities of a carbon-based catalytic membrane for persulfate activation – an important alternative to the application of conventional powder catalysts in water treatment.

To achieve our goal, nitrogen-doped reduced graphene oxide was obtained using melamine as a doping agent (rGO-M), according to the methodology reported elsewhere [1]. Then, a catalytic poly(vinylidene fluoride) (PVDF) membrane, with a good performance for the degradation of fluoroquinolone antibiotics at ppb level in water, was prepared as previously described [2]. To understand the contribution of each membrane component in the reduction of the microbial abundance, the efficiency of the rGO-M–PVDF membrane was compared to that of a PVDF flat membrane, with and without added persulfate, after 6 hours of operation in continuous flow mode using a suspension of faecal indicator bacteria as the feed.

The obtained results allowed us to conclude that the non-catalytic PVDF membrane does not activate persulfate, but retained 98.5% of the initial abundance of *Escherichia coli* and *Enterococcus faecalis.* The antimicrobial properties of rGO-M contributed to remove 99.9% of these faecal indicators when the system was operated with the rGO-M–PVDF membrane without added persulfate. When the system was operated with the catalytic rGO-M–PVDF membrane and persulfate, the microbial load in the treated water was reduced to values below the detection limit, demonstrating the capacity of the catalytic membrane to activate persulfate. Moreover, the amount of microorganisms retained on the membrane decreased, suggesting that this system has enhanced anti-fouling properties.

Similar results were obtained when the proposed treatment system was used to disinfect river water collected nearby the supply of a drinking water treatment plant located in Northern Portugal, with values below the detection limit being obtained for total heterotrophic bacteria, enterobacteria and enterococci in the treated water (even after 24 h operation in continuous flow mode). Moreover, microorganism reactivation and the effect of disinfection on antibiotic-resistance genes (ARGs) were studied. For that purpose, the regrowth of microorganisms and selected genes (16S rRNA, *intI*1, bla_{TEM} and *sul*1) in the treated water, and after 7 days of storage, was evaluated. The results suggest that the proposed system can be a good alternative to other advanced oxidation technologies used for drinking water production.

Acknowledgments

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Ohmic heating-assisted regioselective sulfonation of aniline: synthesis of sulfanilic acid

Vera L. M. Silva[1,*], Mickael R. R. C. Pereira[1], Alejandro F. G. Ribeiro[2] and Artur M. S. Silva[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]Bondalti Chemicals S.A., Rua do Amoníaco Português nº10 Beduído, 3860-680 Estarreja, Portugal.
**verasilva@ua.pt*

The sulfonation of aniline is an important reaction in organic synthesis that originates 4-aminobenzenesulfonic acid, also known as sulfanilic acid (SA), a product of high industrial and economic interest. Large amounts of SA are consumed annually, primarily to produce dyestuffs, but also in the manufacture of fluorescent whitening agents, like tinopal®, used in paper and textile industries and as components of soap and laundry detergent [1]. In addition to the SA, other sulfonated by-products can be formed in the sulfonation reaction such as 2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid, or the disubstituted compounds, 4-aminobenzene-1,3-disulfonic acid and 2-aminobenzene-1,4-disulfonic acid, and finally a trisubstituted compound, the 2-aminobenzene-1,3,5-trisulfonic acid. Several methods have been reported for the sulfonation of aniline but the most straightforward and used one in the industry consists of reacting aniline with an excess of sulfuric acid to produce aniline hydrogen sulfate as intermediate, an exothermic reaction (1st step), followed by splitting of water and migration rearrangement of the sulfonic acid group to the *para*-position (2nd step), by an endothermic reaction, affording SA. This second step requires the use of high temperatures, usually in the range of 165-200 °C, long reaction time, together with very high energy consumption [1]. Thus, any improvements in the regioselectivity and savings achieved in the synthesis of SA are of major economic interest.

In this context, considering the increasing demand for greener synthetic methodologies and novel reactors, and following our interest in ohmic-heating assisted reactions, we studied, for the first time, the sulfonation of aniline with sulfuric acid, as sulfonating agent, using our ohmic heating reactor prototype (PT105908) [2,3]. In ohmic heating, an alternating electrical current of tunable high frequency crosses a conductive reaction medium (which behaves as an *in situ* electrical ohmic heater) by using electrodes in direct contact with the medium. The heat is generated inside the reactor, within the reaction medium, by Joule effect, and does not depend on the heat transfer from an external heat source to the reactor, allowing a fast, volumetric, and uniform *in situ* heating and an increase of reaction fluid and charged species dynamics, which leads, in many cases, to an increase of the overall reaction kinetics, selectivity and yields [3]. Using ohmic heating, we investigated the effect on the sulfonation reaction of various operational conditions, such as the temperature, the stoichiometric amount (equimolar or excess) and concentration of sulfuric acid, the use of vacuum to remove water during the heating, the geometry of the heating electrodes, the reaction time and heating method (ohmic *versus* conventional heating). In our best conditions, sulfanilic acid was obtained with 93% selectivity [4]. There were found energetic advantages related to the heat transfer to the reaction system, such as high heating rate and low thermal inertia, when comparing ohmic heating to the conventional heating. More details about the experiments performed will be presented and discussed in this communication.

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New Trends in Bio-Based Aerogels for CO_2 conversion

A. B. Paninho*, **S. Messias, C. I. Melo, L. C. Branco, A. S. Reis Machado, A. V. M. Nunes**

LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
**inespaninho@fct.unl.pt*

Aerogel bio-based materials have multiple advantages, including high porosity, tunable molecular structures, and environmental compatibility. Besides the ability to achieve a high dispersion of the active phase, it is possible to tune the porous structure of the material in order to facilitate the diffusion of reactants and products to and from the active sites. The utilization of bio-based materials as supports is highly interesting in the context of process sustainability since biopolymer sources are well established, relatively cheap, and accessible at an industrial scale. Alginate is a natural polysaccharide biopolymer mainly derived from brown algae. Due to its biodegradability, low cost, non-toxicity and stability, it is an attractive candidate regarding the greenness of final application [1]. On the other hand, the application of CO_2 as a secure and sustainable supply of carbon for the production of chemicals and fuels is a very active field of research. It explores CO_2 as a C1 building block in alternative to fossil-based resources, bringing carbon back into the value chain and therefore contributing to a circular economy [2]. Due to CO_2 high thermodynamic and kinetic stability, the implementation of process intensification strategies is of crucial importance and plays a decisive role in the economic viability of the technology and perspectives of industrial application. In the case of CO_2 catalytic transformations, the stability of the catalyst, as well as its accessibility and reusability are essential factors to consider [3]. In this work, different alginate aerogels were explored as efficient supporting materials for CO_2 conversion, namely into cyclic carbonates [4] (through cycloaddition reaction to epoxides), synthesis gas [5] (through electrochemical reduction) and methane [6] (through high-pressure hydrogenation). Different techniques were used to immobilize the materials onto the aerogel, depending on the application under study, as shown in Fig. 1.

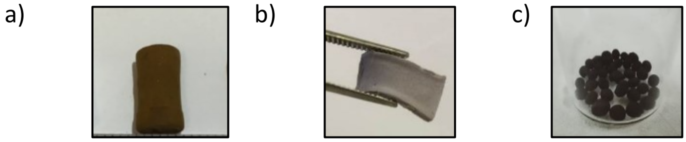

Fig. 1. Different alginate aerogel materials used for CO_2 conversion technologies:
a) cycloaddition reaction b) electrochemical reduction and c) high-pressure hydrogenation.

Final materials were characterised by adsorption–desorption isotherms of N_2 at 77 K, mercury porosimetry, termogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electronic microscopy (SEM). Several tests were performed, and final products analysed by 1H-NMR spectroscopy and gas chromatography. The main advantages brought to the process by the utilization of alginate aerogels as supports were discussed.

Acknowledgments

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AMB33

Extractabilidade de metais pesados en solos urbanos de Santiago de Compostela

María Roo[1,*], Cecilia Herbón[1], Juan Pedro Martín[1,2], María Teresa Barral[1], Remigio Paradelo[1]

[1]Departamento de Edafoloxía e Química Agrícola, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, España
[2]Departamento de Química en Ciencias Farmacéuticas, Universidad Complutense de Madrid, 28040, Madrid, España
**maria.roo@rai.usc.es*

A urbanización e a industrialización poden afectar negativamente ás funcións dos solos urbanos. Entre os problemas máis destacados atópase a acumulación de contaminantes coma os metais pesados. Non é suficiente coñecer as concentracións totais destes contaminantes nos solos, senón que é necesario avaliar a súa extractabilidade para simular a concentración que está dispoñible para as plantas, e polo tanto podería supoñer un risco para a saúde humana ao introducirse na cadea alimentaria. Neste traballo avaliouse a biodispoñibilidade de cinco metais pesados (Pb, Cu, Zn, Ni e Cr) en 55 solos da cidade de Santiago de Compostela con distintos usos (28 mostras de solo con vexetación herbácea, 13 mostras de bosque urbano e 14 mostras de solo de agricultura urbana e periurbana) e formados sobre diferentes litoloxías (granitos, xistos, gneises e anfibolitas) para representar a diversidade edáfica presente na cidade. Todas as mostras proceden dos horizontes superficiais do solo (0-20 cm). Os metais solubles avaliáronse cunha extracción $CaCl_2$ 0,01M [1] e os metais dispoñibles para as plantas cunha extracción en Na_2-AEDT 0,02 M a pH 4,65 [2]. As concentracións dos metais solubles seguiron unha tendencia decrecente Zn > Pb > Ni > Cu > Cr. Só o Zn aparece en forma soluble en cantidades significativas, cunha concentración máxima de 10,6 mg kg^{-1}, sempre por debaixo do 2% do contido total do elemento. Non se observou ningún efecto significativo do uso do solo ou da litoloxía do material de partida. En canto aos metais dispoñibles para as plantas, as concentracións medias para o conxunto de solos seguiron unha tendencia decrecente Pb > Cu > Zn > Ni > Cr. Neste caso, as concentracións de Zn e Cu foron significativamente máis altas en solos de uso agrícola, situados principalmente sobre gneis, o que explica tamén a relación significativa atopada entre a concentración de Cu e esta litoloxía.

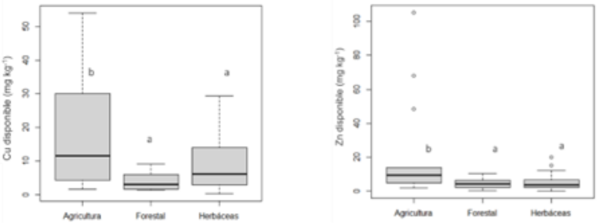

Fig.1. Concentracions de Cu e Zn extraíbles en AEDT en función do uso do solo.

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Lipidic profile of *Salicornia perennis* in different salt marshes of the Ria de Aveiro

N. N. Magni[1,2*], **H. Silva, D. C. G. A. Pinto**[2]

[1]University of Aveiro, CESAM and Biology Department, Aveiro, Portugal
[2]Universidade de Aveiro, LAQV-REQUIMTE and Chemistry Department, Aveiro, Portugal
**magninatasha@ua.pt*

Soil salinization is one of the biggest problems in agricultural production worldwide [1]. Halophytes have many advantages over other plants, such as high productivity in saline and waterlogged environments, nutritional and medicinal properties, phytoremediation, and soil desalination [2]. Secondary metabolites are biosynthesized in response to environmental stress [3], making them rich in proteins, carbohydrates, carotenoids, fibers, oils, and minerals [4]. In addition to being nutritionally interesting, some of these substances also have antioxidant, anti-inflammatory, antitumor, and antimicrobial action [5].

Salicornia perennis Mill. is a perennial halophyte belonging to the Amaranthaceae family [6], forming extensive subshrub patches in the salt marshes of the Iberian Peninsula [7]. In Ria de Aveiro, it inhabits marshes with variable environmental conditions, in which it is subjected to a regime of submersion by tides twice a day [8]. With the general objective of valuing the natural plant resources of the Portuguese coast, we determined the lipophilic profile of *S. perennis* from different marshes of the Ria de Aveiro, and in different organs and phenological states, using GC-MS analysis. These results revealed significant differences in the biocompounds, according to the plants' phenology variations and the physicochemical properties of the sediments where they grow.

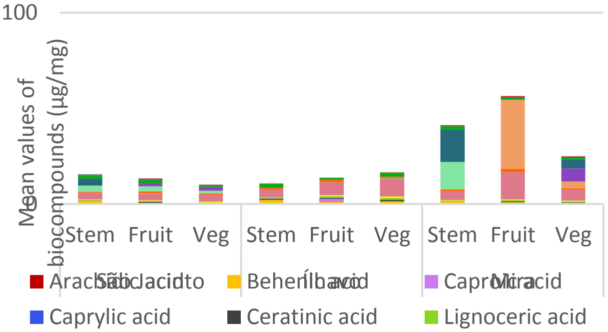

Fig.1. Lipidic profile of *Salicornia perennis* in different organs and phenological stages (fruit: fruiting segments; veg: vegetative segments) from the salt marshes of Ílhavo, Mira and São Jacinto.

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OPTIMIZING THE CHARACTERIZATION OF MICROPLASTICS WHEN IR SPECTROMETRY USING A QUANTUM CASCADE LASER IS USED

Jose M. Andrade[*], **Borja Ferreiro, Adrián López-Rosales, Purificación López-Mahía, Soledad Muniategui-Lorenzo**

Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Universidade da Coruña, 15071 A Coruña, Spain
** Corresponding author: fax: +34-981-167065; andrade@udc.es*

Microplastic particles (MPs) are a new type of pollution, especially prevalent in oceans and coastal areas. MPs are defined as plastic fragments between 5 mm and 1 µm [1]. They are caused mainly by photodegradation and erosion of macroplastics (secondary microplastics), as its production for various industrial and cosmetic applications has been reduced (primary microplastics) [2, 3]. Therefore, accurate identification of plastic particles is crucial for environmental studies in order to monitor polymer pollution.

Common techniques to characterize eventual MPs include chromatograpy, Raman spectrometry and Fourier-transform infrared spectroscopy (FTIR) (either in microreflectance or attenuated total reflectance (ATR) modes) and various types of microspectrometry. All them offer good results although at the expense of very long turnaround times and high laboratory workloads, in particular when faced with big amounts of particles per sample.

Since about 3 years, a novel instrumental IR option was commercialized and represents a breakthrough in IR characterization. Initially developed for stringent pharmaceutical quality control of solid products, a tunable mid-IR quantum cascade laser imaging system (commercialized as LDIR by Agilent) was oriented towards fast-imaging and spectra acquisition. The sample is deposited in a silver-coated microscopy slide. The instrument acquires a “visible image”, where the user can select an area to visualize the absorption of the particles at a specific wavenumber or obtain the spectrum at a point (or a line) over each particle.

This work studies some relevant instrumental parameters that have to be considered in order to optimize the measurement step: (i) The matching criteria (to avoid either false or a lack of identifications), (ii) the measurement area (as it can have an influence in the number of particles detected), (iii) sensitivity (which affect the number of particles identified by the system, that may lead to some artifacts), and (iv) the size of the particles (as it can have an influence on the intensity of the spectral peaks).

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BIOQUÍMICA Y BIOTECNOLOGÍA

Flavonoids as potential anti-obesity compounds:
Inhibition of pancreatic lipase

Sílvia Rocha[1*], Ana T. Rufino[1], Marisa Freitas[1], Félix Carvalho[2], Artur M. S. Silva[3], Eduarda Fernandes[1]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy,
University of Porto, 4050-313 Porto, Portugal
[2]UCIBIO, REQUIMTE, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy,
University of Porto, 4050-313 Porto, Portugal
[3]LAQV, REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**up200702315@ff.up.pt*

Obesity is described as an abnormal or excessive state of adiposity accumulation that could be due to excessive calorie intake [1]. Given the importance of lipids from diet on the onset and development of obesity, the modulation of their absorption can be explored for obesity treatment. For this purpose, one possible target is pancreatic lipase (PL), the enzyme that is responsible for the degradation of 50 to 70% of dietary triglycerides [2].

Presently, only one PL inhibitor – Orlistat – is approved for therapeutic applications. However, it is associated with low efficacy and undesirable side effects, including abdominal distension, flatulence, and oily stools [3]. Thus, the search and development of new effective and safer agents able to control PL catalytic activity as well as the establishment of sensitive techniques and easy-to-apply methodologies for its determination are of great importance for obesity management and control.

Polyphenols are naturally occurring, and structurally diverse compounds characterized by the presence of multiple phenol units. Within these, flavonoids are well known for their diverse biological effects, resulting from their anti-inflammatory, antioxidant, antidiabetic, and anti-obesity activities [4]. This work optimizes the conditions for fluorimetric microanalysis systems based on the enzymatic metabolization of 4-methylumbeliferyl oleate and compares the influence of a set of flavonoids, with hydroxyl and glycosyl substituents, on PL catalytic activity.

The fluorimetric microanalysis system proved to be effective for the evaluation of PL catalytic activity and to determine the inhibitory effect of isolated compounds. Among the tested compounds, it was possible to observe that the glycosylation of the flavonoids seems to cause a decrease in its inhibitory activity. Further studies with more compounds are needed to better disclose the structure activity relationship and consequently their use as potential anti-obesity molecules.

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BB02

Building enzymatic nanoreactors using the IC-Tagging system: a powerful methodology for the stabilization and immobilization of enzymes with industrial interest

Adrián López Teijeiro[1]*, **Daniel Abella López**[1], **Natalia Barreiro Piñeiro**[1], **Gemma Eibes González**[2], **José Manuel Martínez Costas**[1]

[1] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Rúa Jenaro de la Fuente 15705, Santiago de Compostela, España.
[2] Instituto de Investigación Transversal en Tecnologías Ambientales (CRETUS), Rúa Constantino Candeira 15705, Santiago de Compostela, España.
**adrian.lopez.teijeiro@rai.usc.es*

The use of enzymes in the industrial field has been increasing in recent years due to their lower environmental impact and the non-requirement of extreme operating conditions. These biocatalysts have many applications ranging from biofuel production to the development of pharmaceutical products. Thus, biotechnology companies involved in the production of enzymes for these purposes are experiencing a surge in demand, which is expected to increase in the future [1].

Most enzymes with industrial interest have been produced for years in bacteria or yeast representing efficient and optimized expression platforms. However, some enzymes have particular characteristics that compromise their large-scale production by these methods [2]. In order to solve these problems, we propose the use of the IC-Tagging methodology for stabilizing and immobilizing these enzymes, focusing on unspecific peroxygenases (UPOs). This system has been developed in our laboratory and allows us to encapsulate proteins of interest in micro- or nanospheres formed by the viral protein muNS-Mi [3]. Apart from enabling its versatile production in any expression system, the loading of the enzyme in the spheres facilitates its purification and extends its optimal operational conditions. The results obtained show the potential of our methodology for the expression and purification of an encapsulated UPO suitable for use in oxyfunctionalization reactions.

We also demonstrated the feasibility to co-localize some proteins in the aforementioned protein spheres, laying the foundations for the use of the IC-Tagging system in the development of particulate multi-enzyme biofactories (Fig.1). These biofactories could function as nanoreactors allowing simultaneous operation with multiple enzymes as well as scaffolds for the construction of artificial enzymatic pathways.

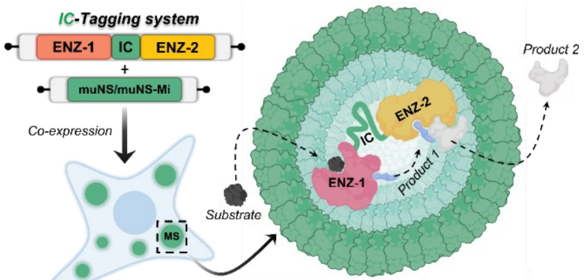

Fig.1. Proposed use of the IC-tagging system for the construction of multienzyme nanoreactors

Acknowledgements
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Soft Free-Standing Membranes made of Chitosan and Alginate as Sustainable Nano-Reservoirs for Controlled Drug/Therapeutics Delivery

Cristiana F. V. Sousa*, Luís P. G. Monteiro, João M. M. Rodrigues, João Borges, João F. Mano

Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
**cristiana.sousa@ua.pt*

The Layer-by-Layer (LbL) assembly technology has been widely used in the last three decades to functionalize virtually any type of surface and precisely engineer robust architectures, with finely tunable properties and functions at the nanoscale, by resorting to a myriad of building blocks exhibiting complementary interactions [1]. In particular, marine-origin polysaccharides, widely directly discarded in the environment due to the processing of marine organisms, are a sustainable renewable resource for the fabrication of nanostructured biomaterials for biomedical applications owing their wide and readily bioavailability, and proven biocompatibility, biodegradability, non-cytotoxicity, and non-immunogenic properties [2]. Chitosan (CHT) and alginate (ALG) have been assembled into multilayered devices owing to their opposite charge nature [3]. However, the insolubility of CHT in physiological conditions limits the use of CHT-based LbL structures in biological, biotechnological and biomedical applications.

Herein, we propose the preparation of electrostatically driven free-standing (FS) multilayered membranes made of water-soluble quaternized CHT (Q-CHT) and ALG biopolymers for the release of model hydrophobic drug molecules. Two different membranes, having either the model drug fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA) as an intrinsic building block [(Q-CHT/ALG/Q-CHT/FITC-BSA)$_{100}$] or added after the assembly of the membranes [(Q-CHT/ALG)$_{200}$/Q-CHT/FITC-BSA], have been produced onto hydrophobic poly(vinyl carbonate) (PVC) substrates (Fig. 1). The morphology, thickness, release rate and *in vitro* biocompatibility of both FS membranes towards human umbilical cord-mesenchymal stem cells was studied, compared, and will be discussed. This work holds great promise for the development of innovative and sustainable biomedical devices for a wide range of bioapplications, overcoming the limitations associated with the use of native CHT biopolymer.

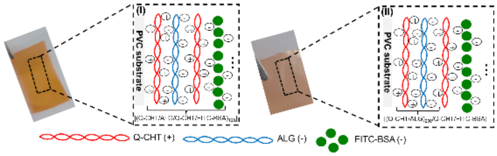

Fig.1. Schematic illustration of the preparation of the two set-ups of FS multilayered membranes: (i) [(Q-CHT/ALG/Q-CHT/FITC-BSA)$_{100}$] and (ii) [(Q-CHT/ALG)$_{200}$/Q-CHT/FITC-BSA] assembled onto PVC substrates *via* electrostatic interactions.

Acknowledgments

The financial support by the Portuguese Foundation for Science and Technology (FCT) through the PhD grants (2020.04408.BD, C.F.V.S.; 2020.06767.BD, L.P.G.M.), and individual Junior Researcher (CEECIND/01363/2018, J.M.M.R.) and Assistant Researcher (2020.00758.CEECIND, J.B.) contracts, is gratefully acknowledged. This work was developed within the scope of the project CICECO – Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds (OE) through the FCT/MEC (PIDDAC).

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Development of an enzyme replacement therapy based on a stabilized version of *Av*PAL using the IC-Tagging system

Daniel Abella López[1,*], Adrián López Teijeiro[1], Natalia Barreiro Piñeiro[1], Gemma María Eibes González[2], José Manuel Martínez Costas[1]

[1]CiQUS Centro Singular de Investigación en Química Biológica y Materiales Moleculares, Rúa de Jenaro de la Fuente s/n 15705, Santiago de Compostela, España
[2]CRETUS Centro de Interdisciplinar de Investigaciones en Tecnologías Ambientales, Rúa de Constantino Candeira 15705, Santiago de Compostela, España
**Daniel.abella@rai.usc.es*

Phenylketonuria is the most common hereditary defect in amino acid metabolism and is characterized by the presence of excessive levels of phenylalanine in blood and tissues. Currently, the only available treatment of this pathology is based on a strict diet without phenylalanine [1].

Our work proposes the use of the IC-Tagging system patented in our laboratory to develop an orally administered enzyme replacement therapy. Based on the development of a stabilized version of the enzyme phenylalanine ammonium lyase from *Anabaena variabilis* (*Av*PAL), which can reduce the phenylalanine levels of patients; thus avoiding the neurological disorders characteristic of the pathology [1]. The IC-Tagging methodology is a protein labeling platform based on the use of the avian reovirus-derived muNS-Mi protein. This system is able to produce protein micro- or nanospheres (MS or NS) that can be loaded with proteins of interest in any expression system through their tagging with a tag called IC [2].

Our results suggest that it is possible to use our system to produce nanospheres loaded with the active *Av*PAL enzyme maintaining their function and correct folding in an inexpensive and simple way. Moreover, it is possible to coat the nanospheres with different polymers to increase stabilization and avoid degradation and immune response without losing specific activity (Fig.1).

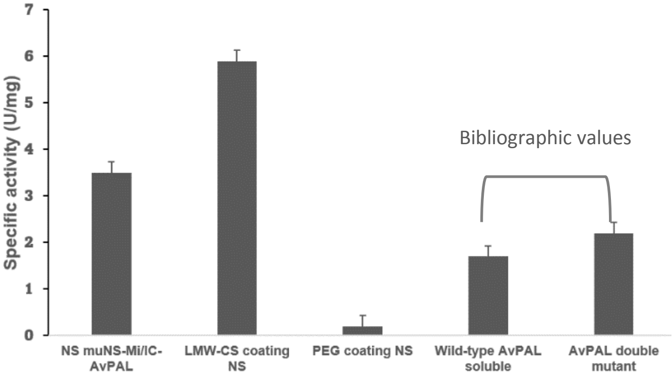

Fig.1. Specific activity of *Av*PAL encapsulated in NS and coating NS with low molecular weight chitosan (LMW-CS) or polyethylene glicol (PEG) compared with bibliographic values.

Acknowledgments
This research was funded by the Spanish Ministry of Science and Innovation. Special thanks to all members of the Molecular Virology Group (CiQUS).

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Downstream processing of L-asparaginase through silica-based supported ionic liquid-like phase materials

João C. F. Nunes[1,*], Mafalda R. Almeida[1], Valéria C. Santos-Ebinuma[2], Márcia C. Neves[1], Mara G. Freire[1], Ana P. M. Tavares[1]

[1]CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Department of Engineering of Bioprocesses and Biotechnology, School of Pharmaceutical Sciences, São Paulo State University (UNESP), 14800-903 Araraquara, Brazil
**jcfn@ua.pt*

L-asparaginase (ASNase) is an amidohydrolase enzyme widely applied as an anticancer agent in the treatment of lymphoproliferative disorders, e.g., acute lymphoblastic leukemia (ALL), lymphomas, and natural killer cell tumors, as an acrylamide reduction agent in starch-rich foods cooked at high temperatures, and as a biosensor for L-asparagine detection and monitoring [1]. ASNase is extensively distributed in nature, e.g., microorganisms, plants, and animals; however, most commercial ASNase are from recombinant microorganisms, whose production can be performed through fermentation. Nonetheless, its downstream processing accounts for up to 80% of total production cost [2]. Thus, the development of a novel cost-effective purification process is of emerging concern to allow its widespread use.

The main goal of this work is to develop a novel cost-effective downstream process for ASNase from complex recombinant *Bacillus subtilis* cell lysate obtained through ultrasound sonication. Silica-based supported ionic liquid-like phase (SSILLP) materials comprising quaternary ammonium and chloride as counterions, previously used to produce ASNase-SSILLP bioconjugates through simple adsorption of commercial ASNase [1], were investigated as cost-effective ASNase purification supports through a simple adsorption method. Specific experimental conditions, e.g., medium pH and solid/liquid ratio, were optimized through Response Surface Methodology regarding ASNase purity. Through this approach, process costs, energy consumption, and waste produced, might be significantly reduced, leading to the ASNase price decrease, thereby enabling its wider application.

Agradecimientos

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This work was supported by the project POCI-01-0145-FEDER-031268-funded by FEDER through COMPETE2020, and by national funds (OE) through FCT/MCTES, and by FAPESP (2018/06908-8). Ana P. M. Tavares and Márcia C. Neves acknowledge FCT for the research contract CEECIND/2020/01867 and CEECIND/00383/2017, respectively. João C. F. Nunes acknowledges SPQ and FCT for the PhD fellowship (SFRH/BD/150671/2020).

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CATÁLISIS Y FOTOCATÁLISIS

Ionic Liquid-based POM@ZIF-8 as a catalyst for simultaneous desulfurization and denitrogenation processes

Dinis F. Silva[1,*], **Alexandre M. Viana**[1], **Isabel Santos-Vieira**[2], **Salete S. Balula**[1], **Luís Cunha-Silva**[1]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
[2]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
**josedinis.silva@fc.up.pt*

An effective and sustainable process capable to execute simultaneously desulfurization and denitrogenation of fuels is in fact an actual need for the refinery industry. The key to achieve this goal is the parallel oxidation of sulfur and nitrogen compounds present in fuels using active and recyclable catalysts.[1] Polyoxometalates (POMs) are described for their high catalytic efficiency as homogeneous catalysts in simultaneous oxidative desulfurization and denitrogenation of model fuel oils.[2] This work presents a novel heterogeneous catalyst prepared via encapsulation of an imidazolium-based polyoxometalate into ZIF-8 framework ([BMIM]PMo12@ZIF-8). This composite material has shown exceptional catalytic efficiency towards the oxidative desulfurization and denitrogenation of a model fuel containing various sulfur and nitrogen compounds. The catalyst was able to completely remove all these compounds after only 60 minutes and the reutilization of the catalytic system was studied for ten consecutive cycles without showing any loss of efficiency. This work presents the first incorporation of an ionic liquid-based POM into ZIF-8. The novel material was successfully used as catalyst to simultaneous remove sulfur and nitrogen from a multicomponent model fuel.

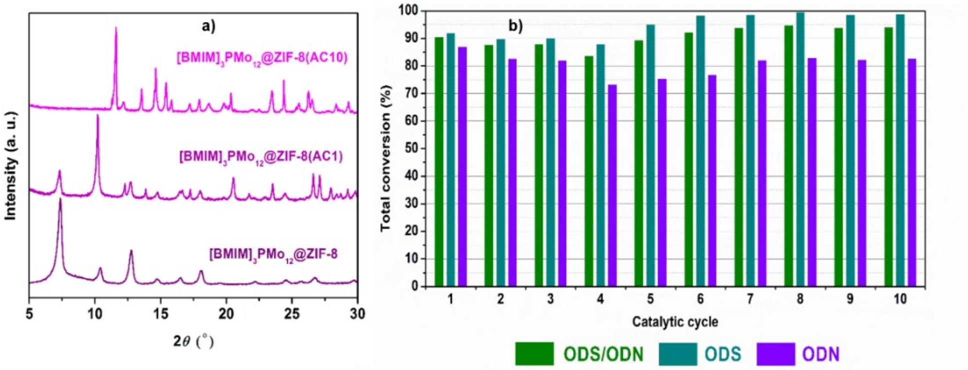

Fig.1. Scheme of a) PXRD patterns of [BMIM]PMo$_{12}$@ZIF-8 material before catalytic utilization, isolated after 1 cycle (AC1) and after 10 catalytic cycles (AC10) and b) Reutilization performance of [BMIM]PMo$_{12}$@ZIF-8 over 10 cycles combining desulfurization and denitrogenation processes to treat a multicomponent model fuel.[3]

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CAT02

Catalytic membranes based in polyoxometalates for fuel desulfurization

Catarina Dias[1,*], **Rui G. Faria**[2], **Salete S. Balula**[2]

[1] REQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
[2] REQUIMTE/LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
*up201804900@edu.fc.up.pt

Fuels are constituted by sulfur components that pose a danger to the environment when burned, which implemented the application of sulfur regulations. In order to answer these demands, processes that allow the desulfurization of fuels are essential, such as hydrodesulfurization (HDS) and oxidative desulfurization (ODS). [1]

The preparation of a catalytic membrane, through polyoxometalate immobilization in supporting materials, and application as heterogeneous catalysts in the oxidative desulfurization process (ODS) was studied. The use of heterogeneous catalysts allows better separation and removal from the reaction, and furthermore facilitates their recovery and recycling. [2]

The membranes were prepared by immobilizing phosphomolybdic acid ($H_3PMo_{12}O_{40}$) in a polymer matrix. The reactions were performed using a model oil composed of approximately 500 ppm of refractory sulfur components (1-benzothiophene, dibenzothiophene, 4-methyldibenzothiophene and 1,6-dimethyldibenzothiophene).

The catalytic membranes showed satisfactory catalytic performance, allowing further research of their application in the oxidative desulfurization process.

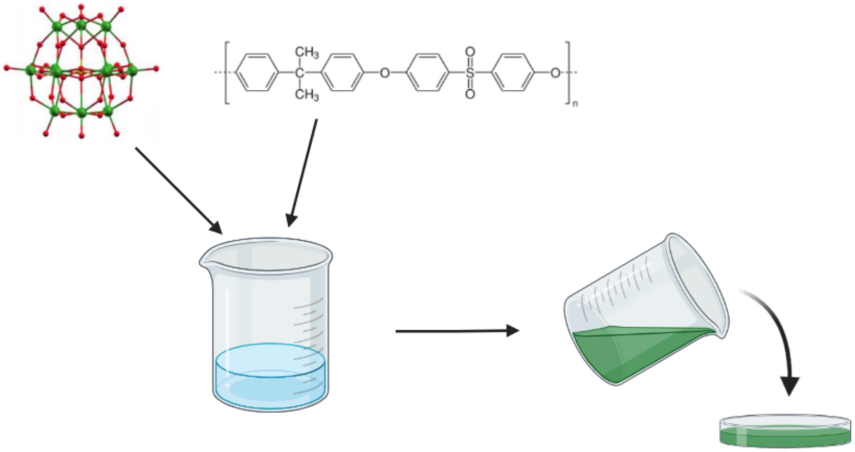

Fig.1. Scheme of the catalytic membrane preparation used in this work.

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Metal Organic Frameworks as adsorbents with catalytic properties promoting Advanced Oxidation Regeneration

Aida M. Díez[1],*, Clara Gómez-González[1], Marta Pazos[1], M. Ángeles Sanromán[1]

[1]CINTECX, Grupo de Bioingeniería y Procesos Sostenibles, Departamento de Ingeniería Química,
Campus Lagoas-Marcosende, Universidade de Vigo, 36310 Vigo, Spain
*adiez@uvigo.es

Pharmaceutical compounds are detected on wastewater treatment plant effluents due to their toxicity and stability in biological treatments [1]. Adsorption has been proposed as a quick, simple and efficient procedure to cope with pharmaceuticals. However, spent adsorbents should be reused in order to avoid disposal problems related to inefficient space usage and pollutants leaching.

Advanced Oxidation Processes (AOPs) have been used as an alternative for adsorbent regeneration (Advanced Oxidation Regeneration), as they are based on the generation of radical species which attack efficiently the organic matter in the porous matrix. Among AOPs there is the i) Fenton process which is the catalytic decomposition of H_2O_2 in presence of transition metal so HO· is generated ii) sulphate-based degradation, where peroxymonosulfate (PMS) or persulfate are activated by carbon or metals [2] or iii) photocatalysis where radiation activates a semiconductor therefore oxidative and reduction reactions take place [3].

For the generation of those radicals, the adsorbent can present the presence of metals in order to favour AOPs. Consequently, Metal Organic Frameworks (MOF), which are porous organic structures with metallic centres, are hereby presented as perfect catalytic adsorbents [5] Consequently, NH_2-MIL-101(Fe) [4], NH_2-MIL-125(Ti) [3] and MIL-53(Al) [5] were synthesized to be tested on diclofenac sodium (DS) removal.

These synthesized MOFs not only showed high DS adsorption but also, they were recovered by different AOPs (Table 1). The structural and catalytic information of the MOFs was evaluated by physical and chemical characterization and electrochemical analysis. All of that demonstrated these MOFs are porous and photo-electrochemically active (Table 1).

Table 1. MOF uptakes and regeneration (%) after the application of different AOPs.

MOF	Uptake (mg/g)	Photocatalysis		PMS	H_2O_2
		Visible	UV		
NH_2-MIL-125(Ti)	724.98	60.87	59.79	47.03	62.14
NH_2-MIL-101(Fe)	481.73	30.27	64.66	79.99	62.40
MIL-53 (Al)	598.30	6.40	64.19	28.72	35.37

Moreover, the AOPs working conditions were optimized and consequently, the optimal H_2O_2 dosage was 14.5 mM, the best PMS concentration was 60.5 mM and the photocatalysis process should be applied for 6 h in order to attain the greatest performance. Under these conditions, up to three adsorption-regeneration cycles were done and less than 20 % detriment was detected. This demonstrates that MOFs can be efficiently used for the treatment of pharmaceutical effluents.

Acknowledgements

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Shrimp shells derived electrocatalysts towards oxygen reduction reaction

Renata Matos[1,*], **Jorge Manuel**[1], **Inês S. Marques**[1], **Andreia F. Peixoto**[1], **Diana M. Fernandes**[1]

[1]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
** renata.matos@fc.up.pt*

Electrochemical energy conversion devices such as fuel cells and metal-air batteries have arisen as promising alternatives to fossil fuels combustion. However, both technologies rely on several electrochemical processes, including oxygen reduction reaction (ORR), whose sluggish kinetics and large overpotentials hinders their practical application [1]. As so, the development of high-performance and cost-effective electrocatalysts is fundamental.

Carbon-based electrocatalysts have been successfully applied towards ORR, aiming to the replacement of conventional precious metal catalysts [2]. Recently, carbon materials obtained from the pyrolysis of biomass, known as biochars, have attracted interest as highly sustainable catalysts, due to their unique physical-chemical properties, renewable feedstock, and low production cost [3]. While biochars have significant catalytic activity, it is usual to enhance their electrochemical properties via heteroatom doping (e.g, N, S, P) [3]. Furthermore, biochars are excellent supports for the incorporation of catalytic active metal oxides, producing high-performance, low-cost and stable catalysts towards ORR [3].

In this work, a highly porous biochar was prepared from shrimp shell waste, N-doped using a solvent-free mechanochemical approach and modified with several metal oxides (Co_3O_4, $NiCo_2O_4$ or $Ni_{0.5}Mn_{0.5}Fe_2O_4$) via in situ co-precipitation under mild conditions. The prepared materials were extensively characterized by FTIR and Raman spectroscopies, XPS and SEM-EDS. All biochar-based electrocatalysts displayed considerable activity towards ORR in alkaline medium. The N-doping led to an enhanced selectivity towards the 4 electron-pathway and lower Tafel slope, although with a decreasing of the diffusion limited current density. The introduction of metal oxides into the N-doped biochar also had a significant effect on the catalysts' behavior, namely on their selectivity, Tafel slopes, onset potentials and diffusion-limited current densities. In particular, the N-doped biochar/Co_3O_4 hybrid showed remarkable selectivity, low Tafel slope (65.6 mV dec^{-1}), onset potential of 0.78 V vs. RHE and considerable long-term stability.

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Self-assembled binary structures of Fe(III) and metal-free porphyrins for sunlight-assisted catalytic hydrogenation

Gabriela A. Corrêa, Marcelo P. Loureiro, Iwona Kuźniarska-Biernacka, Cristina Freire, Susana L.H. Rebelo*

LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal.

**susana.rebelo@fc.up.pt*

The attainment of reduction reactions using environmentally friend conditions and non-noble metal-based catalysts is an important goal for Sustainability. In recent years, biomimetic iron (III) based materials have been gaining attention as reduction catalysts for diverse applications [1].

Nanostructured binary materials have been prepared by ionic self-assembly of oppositely charged (metallo)porphyrins, in a simple and eco-sustainable way. These materials form as precipitates in water and at room temperature and have relevant catalytic properties [2]. In this work, binary materials of Fe(III) and metal-free porphyrins were prepared by ionic self-assembly and tested in the mimics of the six-electron reduction activity of nitrite reductase (Fig.1) [3]. The reduction of 4-nitrophenol to 4-aminophenol, in the presence of $NaBH_4$ and under simulated solar light irradiation, was carried out and a structure effect could be observed. For materials built with two oppositely charged Fe(III) porphyrins, the increase in catalytic activity was temperature-dependent, whereas in a material built with a metal-free porphyrin and a Fe(III) porphyrin, the activity was dependent on visible-light irradiation. This latter material shows the highest catalytic activity of 388 min^{-1}�g^{-1}, after an induction time of 7 min, and shows good performance after reuse studies [3].

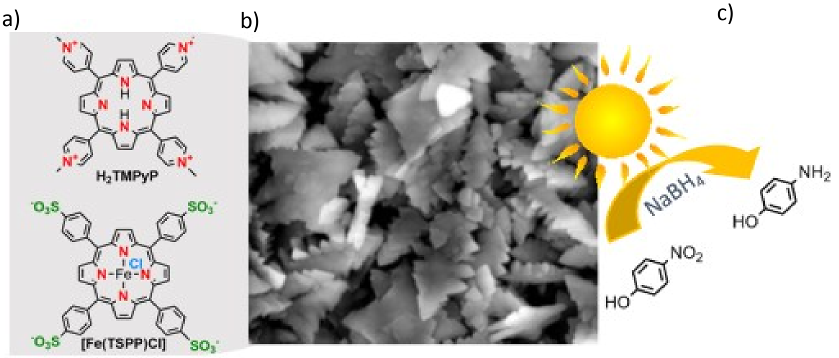

Fig.1. a) Positive metal-free and negative iron (III) porphyrins used as tectons in ionic self-assembly reactions; b) SEM image of the material with the highest catalytic activity; c) Catalytic hydrogenation of 4-nitrophenol assisted by sunlight.

Acknowledgments

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CAT06

Binary Mn(III) and Fe(III) porphyrin nanostructured materials in catalytic hydrogenations assisted by sunlight

Gabriela A. Corrêa*, Susana L.H. Rebelo, Baltazar de Castro

LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal.
**up201900612@edu.fc.up.pt*

The ionic self-assembly of oppositely charged porphyrins allows the preparation of binary materials with well-defined shapes and sizes [1]. These materials can be easily obtained in an eco-sustainable way, as they form as precipitates in aqueous solution and at room temperature. The assembly of porphyrins carrying different substituents and metal ions affords materials, in which cooperative processes can occur between the positive and negative tectons [1]. As such, novel or improved properties can be obtained and be relevant in biomimetic and eco-sustainable reactions.

In this work, binary nanostructured materials carrying positive and negative iron (III) and manganese (III) porphyrins (Fig. 1) were prepared by ionic self-assembly and characterized by SEM, XPS and XRD. The materials were tested in the hydrogenation of 4-nitrophenol to 4-aminophenol in water, using $NaBH_4$ as a reductant and in the presence and absence of simulated solar light. This reaction allows the transformation of a harmful pollutant into a useful intermediate for the synthesis of pharmaceuticals and is relevant in the context of a circular economy [2].

The catalytic activity of the binary materials is improved relatively to that of the original metalloporphyrins. After 5 minutes a 90% conversion was obtained for material [Fe/Mn] carrying Fe(III) and Mn(III) porphyrins as positive and negative tectons, respectively. This material can be reused in successive catalytic cycles and until the 5th cycle with no significant loss of catalytic activity. The observed catalytic performance is comparable to that of catalysts based on noble metals, which are significantly more expensive and scarcer [3].

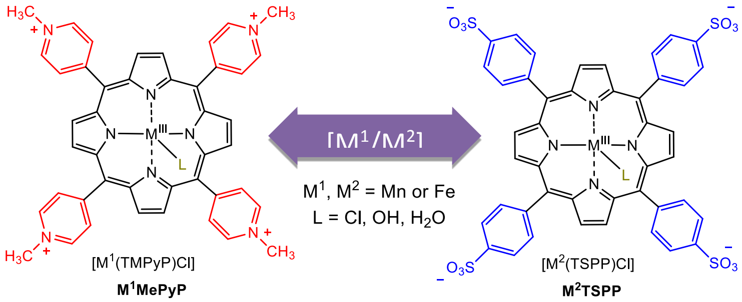

Fig.1. Positive and negative iron (III) and manganese (III) porphyrins used as tectons in the ionic self-assembly reactions.

Acknowledgments
We thank FCT/MCTES (Fundação para a Ciência e Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior) for financial support through the projects UIDB/50006/2020 and REQUIMTE/EEC2018/30 (SLHR).

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Fabrication of a new $Fe_3O_4@TiO_2$ composite as a magnetic recoverable photocatalyst for degradation of water pollutants

Jorge López Gallego[1*], Ana Rey Barroso[2], Vicente Montes Jimenez[1], Pedro M. Álvarez Peña[1]

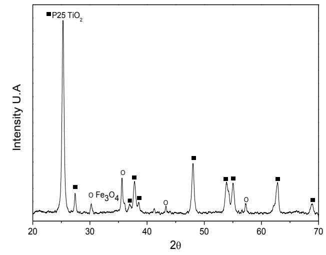
[1]Instituto Universitario de Investigación del agua, Cambio Climático y Sostenibilidad (IACYS), Av. de la Investigacións/n, Badajoz, España
[2]Universidade de Coimbra, 3004-531, Coimbra, Portugal
**jorgelg@unex.es*

Los procesos avanzados de oxidación (PAOs) constituyen una tecnología de tratamiento de contaminantes del agua basada en la generación de radicales libres y otras especies de gran poder oxidante. Los PAO fotocatalíticos mediante tecnologías solares han cobrado gran interés en los últimos años. Entre ellos cabe destacar la oxidación fotocatalítica

La ozonación fotocatalítica y el sistema foto-Fenton. En relación con ellos, los principales retos actuales se centran en la fabricación de catalizadores estables, eficientes y fácilmente separables del medio acuoso.

En el presente trabajo se expone un novedoso proceso de síntesis verde donde se magnetiza Aeroxide TiO_2-P25 (Evonik) mediante oxidación precipitativa de Fe(II) en medio acuoso y a temperatura ambiente. Como agente director de la síntesis se emplea ácido tereftálico que se recupera y reutiliza en el proceso.

Así, se obtienen catalizadores magnéticos ($Fe_3O_4@TiO_2$) compuestos mayoritariamente por magnetita (Fe_3O_4) y TiO_2. Además de la optimización de la síntesis, se llevó a cabo una caracterización de los sólidos mediante numerosas técnicas (Difracción de rayos X (DRX), Fluorescencia de rayos X, microscopía electrónica de barrido (SEM), medida de la susceptibilidad magnética, etc), las cuales demuestran la estructura homogénea del sólido, su alto grado de magnetización y la presencia de Fe_3O_4. Se comprobó también la estabilidad del sólido a diferentes valores de pH y, especialmente, en medios fuertemente oxidantes. La actividad fotocatalítica se comprobó usando Metoprolol (MTP) como contaminante objetivo en reacciones de oxidación fotocatalítica, Ozonación Fotocatalítica y foto-Fenton bajo radiación solar simulada, demostrándose un buen desempeño del catalizador en estos procesos tras varios ciclos de reutilización.



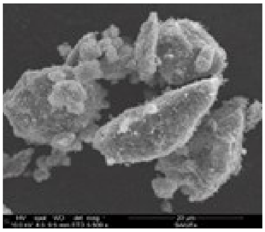


Fig. 1. DRX y SEM del catalizador $Fe_3O_4@TiO_2$

Agradecimientos

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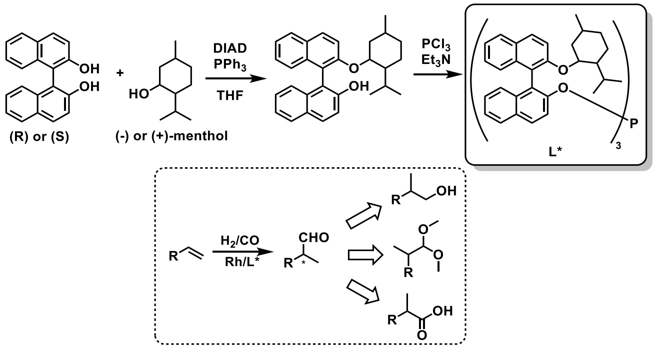
Hydroformylation-based reactions using chiral binaphthyl monophosphite ligands

Alexandre P. Felgueiras,[1*], **Fábio M. S. Rodrigues**,[1] **Rui M. B. Carrilho**[1], **Mariette M. Pereira** [1]

[1]CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal;
[1]Institución, Dirección, Ciudad, País
*alexandrefel42@gmail.com

The development of sustainable reactions is increasingly more relevant in the scientific community, due to the importance of reducing the environmental impact of current chemical processes. Catalytic hydroformylation of olefins is a widely used reaction in the chemical industry to obtain aldehydes as extremely versatile intermediates, which can be transformed into a myriad of different valued added products[1]. By developing hydroformylation-based sequential reactions, we can effectively reduce the number of steps in the reaction processes, and in this way, increase the sustainability of the whole process[1,2]. The use of C_3-symmetric BINOL based monophosphites have shown great potential in catalysis[3]. Various examples, already developed by our group, have demonstrated their efficient application catalytic carbonylation[4] and hydroformylation reactions[5].

In this work, we describe the synthesis of four diastereomeric BINOL-based monophosphite ligands in two steps. We also present our recent results of their application in asymmetric hydroformylation of olefins and the subsequent derivatization of the aldehydes **(Scheme 1)**. The effects of the substrate structure, reactions conditions (CO/H_2 pressure, temperature) and ligand chirality on the catalytic activity and selectivity will be appraised and discussed.



Scheme 1: Synthesis of chiral binaphthyl monophosphites and their application in hydroformylation-based reactions.

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Graphitic carbon nitride coated onto alumina foams as an efficient supported visible-active photocatalyst for the degradation of pharmaceutical substances in water

Ana M. Chávez[1,2,3*], **André Torres-Pinto**[1,2], **Pedro M. Álvarez**[3], **Cláudia G. Silva**[1,2], **Joaquim L. Faria**[1,2], **Adrián M.T. Silva**[1,2]

[1] LSRE-LCM - Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2] ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[3] IACYS - Instituto del Agua, Cambio Climático y Sostenibilidad, Universidad de Extremadura, Avda. Elvas s/n 06006, Badajoz, Spain
**achavez@fe.up.pt*

Graphitic carbon nitride (gCN) is a metal-free photocatalyst widely investigated due to its high photocatalytic activity and chemical stability under visible-light illumination [1]. Most of the research has been performed with powdered gCN suspended in water; however, immobilized photocatalysts are more suitable solutions for the scale-up of these processes [2].

This study is focused on the simultaneous *in-situ* synthesis and immobilization of gCN onto reticulated non-porous alumina foams (AF) for the photocatalytic removal of pharmaceutical substances from water. Graphitic carbon nitride was successfully deposited onto AF by thermal condensation of C and N rich precursor (urea) in both solid and liquid phase, a gCN strong adhesion to the AF support being achieved (24 ± 5 mg gCN/g AF). Then, this material (labeled as gCN-F) was exposed to visible LED radiation in batch conditions, showing photocatalytic activity for tramadol (TMD) degradation (Fig 1.A). The process performance is enhanced by adding hydrogen peroxide (*i.e.,* H_2O_2-assisted photocatalysis), a complete tramadol degradation being achieved in 120 min (Fig. 1.B shows the H_2O_2 evolution). Moreover, comparing the two H_2O_2-assisted photocatalytic processes, higher nitrate concentration is obtained in the liquid phase in the presence of gCN-coated material (Fig. 1.C), probably due to the decomposition of H_2O_2 into radical oxygen species that attack the organic pharmaceutical molecules, releasing nitrate.

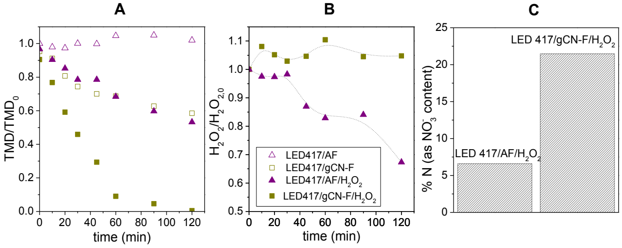

Fig.1. Evolution of normalized A) TMD and B) H_2O_2 concentrations with time and C) conversion of organic nitrogen into nitrate. Conditions: Max. wavelength: 417 nm, irradiance: 550 Wm^{-2}, TMD_0: 20 mgL^{-1}, volume: 50 mL (batch), pH: free, H_2O_2: 50 $mmolL^{-1}$ (when needed), AF load 2.7 ± 0.3 g.

Acknowledgments

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Hydrochars dopados con nitrógeno para la activación del peroximonosulfato: evaluación para el tratamiento de aguas residuales

Silvia Escudero-Curiel[1, *], **Xacobe López**[1], **Marta Pazos**[1], **Ángeles Sanromán**[1]

[1]CINTECX. Universidade de Vigo, Departamento de Ingeniería Química. Campus As Lagoas-Marcosende, 36310 Vigo, España
**sescudero@uvigo.gal*

Los efectos de la presencia, cada vez más extendida, de productos farmacéuticos en los medios acuáticos son objeto de intensa investigación y debate debido a su potencial para causar efectos adversos en los organismos acuáticos y en la salud humana. Por tanto, es evidente que la búsqueda de tratamientos eficaces para purificar las aguas contaminadas es imperativa. Los Procesos de Oxidación Avanzada (POAs) se han aplicado con éxito en el tratamiento de aguas para contaminantes orgánicos [1]. De entre estas técnicas, el peroximonosulfato (PMS) ha sido foco de atención debido a su reactividad selectiva con los compuestos orgánicos y su excepcional rendimiento en un amplio rango de pH. El PMS produce radicales hidroxilo y sulfato al activarse, pero los catalizadores más utilizados se basan en metales de transición, que acumulan problemas de lixiviación y toxicidad. En este sentido, se están investigando nuevos catalizadores sin metales para superar estos inconvenientes. Los materiales sin metales basados en carbono tienen unas propiedades fisicoquímicas inusuales que los hacen interesantes para un sinfín de aplicaciones, como electrodos, adsorbentes amables con el medio ambiente y catalizadores. Los residuos agroindustriales son grandes precursores verdes para obtener materiales carbonosos por medio de procesos de carbonización hidrotermal. Además, el dopaje de estos materiales carbonosos con otros heteroátomos, especialmente nitrógeno, añade más sitios activos en la estructura del carbono, lo que podría mejorar la actividad catalítica [2]. En este estudio, se realizó la producción y posterior funcionalización con nitrógeno de varios *hydrochars*. Las funcionalizaciones fueron llevadas a cabo empleando varios niveles de nitrógeno y con diferentes agentes reticulantes, glutaraldehído y 1-etil-3-(3-dimetilaminopropil)carbodiimida hidrocloruro (EDC) para ser probados como activadores de PMS. Posteriormente, se realizaron varios ensayos para determinar la dosis óptima, utilizando como contaminantes modelo un compuesto farmacéutico, fluoxetina, y un tinte, Reactive Black 5, para evaluar el proceso. En base a los resultados logrados, se puede concluir que estos *hydrochars* dopados con nitrógeno son prometedores y se ha comprobado que en mecanismo de degradación era la vía no radicalaria.

Agradecimientos

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Tri-hybrid catalyst combining polyoxometalates, MOF and silica for the desulfurization of heavy fuel oil

Simone C. Fernandes[1*], Baltazar de Castro[1], Salete S. Balula[1], Luís Cunha-Silva[1], Pedro L. Llorente[2]

[1]LAQV/REQUIMTE, Faculty of Sciences, University of Porto, 4169-007, Porto, Portugal
[2]Universidad Rey Juan Carlos, Madrid, Spain
**up201603496@fc.up.pt*

The combustion of sulfur-based compounds, present in fuels, results in the emission of hazardous gases, namely, sulfur oxides (SO_x). Currently, strict legislation has been stablished demanding low sulfur limits for road fuels (S < 10 ppm) and for marine fuel (S < 500 ppm).[1] The traditional method for the removal of sulfur in fuels, hydrodesulfurization (HDS), is well established but is based on expensive technology, requiring severe experimental conditions to achieve high efficiency in maritime fuels which are based in heavy fuel oils (HFOs). Therefore, effort has been put to develop alternative and/or complementary methods, for example, oxidative desulfurization (ODS). Through ODS, sulfur refractory compounds can be effectively removed from fuels at moderate temperature and atmospheric pressure. ODS requires the activation of the oxidant, e.g., H_2O_2, by a catalyst.[2]

Polyoxometalates (POMs), i.e., $H_3PMo_{12}O_{40}$ (PMo_{12}) show high catalytic performance in ODS; however, they are highly soluble in catalytic media, behaving as homogeneous catalysts. Therefore, their heterogenization in solid supports, such as metal-organic frameworks (MOFs), leads to active heterogeneous catalysts with robustness and easy recovery from reaction. The effectiveness of POM@MOF catalysts has been shown in previous studies.[3] Our research group recently prepared a novel composite, PMo_{12}@MOF-808, which revealed to be an active and recyclable catalyst for ODS of a model fuel.[4] However, the sturdiness provided by MOFs isn't always sufficient to ensure structure stability and prolonged recycling cycles of catalysts under severe reactional media, such as the treatment of HFO.Thus, the robustness of POM@MOF catalysts has been enhanced by the preparation of composites combining MOFs and mesoporous silicas, MOF@silica.[5] The incorporation of MOFs in silicas allows the final composite to retain micropores from the MOF, selective in size and shape for certain molecules; and mesopores from the silica, that allow access to active sites, improving product and substrate diffusion.[6]

Reported studies on hybrid materials combining POM, MOF and silicas are very scarce.[7] In this work, a novel tri-hybrid material was prepared by incorporation of the composite, PMo_{12}@MOF-808, in a mesoporous silica SBA-15. Two different methods were followed: solvothermal and incipient wetness impregnation. The composites were characterized by FTIR, PXRD, SEM-EDS and ICP-OES and tested as catalyst for ODS of a multicomponent model fuel containing refractory sulfur compounds, using H_2O_2 as oxidant and the ionic liquid [BMIM]PF_6 as extraction solvent. The recycling capacity and stability of the heterogeneous catalyst were also investigated. Furthermore, the activity and stability of the composite prepared by IWI was tested for ODS in a more complex model fuel, representative of a HFO.

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Electrocatalytic performance of biochar-based catalysts

Inês S. Marques[1*], Andreia F. Peixoto[1], Diana M. Fernandes[1]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences,
University of Porto, 4169-007 Porto, Portugal
**up201608306@fc.up.pt*

The current and energy crisis and war has stimulated new measures to reduce energy consumption and the development of viable, sustainable, and clean energy solutions for energy storage and conversion. The development of these technologies such as fuel cells and water splitting devices, aim to reduce the effects of energy demand [1].

In the reactions of oxygen - the O_2 reduction (ORR) and evolution (OER) reactions, conventional electrocatalysts (ECs) are based on noble metals and their oxides, such as Pt, RuO_2, and IrO_2. However, these have poor stability under operating conditions, as well as high cost and scarcity, seriously limiting their large-scale commercial applications [2]. As an alternative, the development of a new generation of sustainable, stable and affordable high-quality materials such as biomass can be a solution for this problem.

In this context, the work developed aimed to design and prepare a new generation of electrocatalysts, prepared from natural and renewable sources (biochar obtained from vineyard pruning waste) to act as electrocatalysts for the demanding electrochemical reactions ORR and OER. It can be easily prepared from the thermochemical degradation of biomass and due to the unique chemical structure, it can be easily activated or functionalized. All materials prepared demonstrated moderate ORR electrocatalytic performance in alkaline medium with diffusion-limiting current densities between -3.48 and -1.27 mA cm^{-2} and potential onset values of $0.88 \geq E_{\text{onset}} \geq 0.66$ V vs. RHE. The materials also presented moderate OER electrocatalytic performances in alkaline medium, with overpotential values between 0.48 and 0.63 V vs. RHE and maximum current densities between 0.28 and 42.60 mA cm^{-2}.

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Promoted Ni/BEA catalysts for dry reforming of methane

José Ferreira, Ana C. Ferreira, Carmen Bacariza*

Centro de Química Estrutural, Departamento de Engenharia Química, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049 001 Lisboa, Portugal

**maria.rey@tecnico.ulisboa.pt*

An important effort is nowadays required for increasing the share of renewables in the global energy system in order to accomplish the international climate goals. In this context, using sewage sludge, agricultural and crop residues, animal dung, industrial organic wastes, or wastewaters for the production of biogas through anaerobic digestion constitutes a promising strategy. Biogas, composed mainly of CH_4 and CO_2, can be upgraded to biomethane and used as synthetic natural gas, representing an attractive renewable carbon source whose exploitation is advantageous from both financial and environmental points of view [1]. Alternatively, biogas could be used to produce syngas (mixture of H_2 and CO) through dry reforming of methane, DRM: $CO_2 + CH_4 \rightarrow 2CO + 2H_2$, $\Delta H^0_{298K} = +247$ kJ/mol), an important feedstock in the synthesis of oxygenated chemicals (e.g. methanol), acetic acid, or fuels (e.g. long chain hydrocarbons) [1]. Despite its interest, DRM is still an immature industrial process due to its highly endothermic nature, requiring high operating and investment costs, in addition to catalysts deactivation due to sintering and carbonaceous species formation [2].

Current catalysts for this process may contain noble (e.g., Ru, Rh, Pt) or transition (e.g., Ni, Co) metals supported over CeO_2, La_2O_3, ZrO_2, MgO, SiO_2, Al_2O_3, MOFs or zeolites [2-4]. Noble metals are known to resist deactivation, but their high cost and low availability limit their industrial application [2,3]. As such, the cost-effectivity of Ni catalysts motivates further developments on the enhancement of their properties in order to design highly active, selective and stable materials. Several types of Ni-based zeolites have been applied in DRM due to their easily tuneable properties [2-4]. However, systematic studies are still scarce and motivate further research in this area.

Therefore, in the present work a series of Ni-based BEA zeolite was synthesized by incipient wetness impregnation, characterized by powder X-ray diffraction (XRD), N_2 sorption, temperature programmed reduction with H_2 (H_2-TPR), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM), and tested towards thermal dry reforming of methane using a fixed-bed reactor (0.200 $g_{catalyst}$, 290 ml.min^{-1} of $CO_2/CH_4/N_2$ mixture, 1 atm, 450 to 700 ºC). The effects of Ni loading (5, 10 and 15 wt.%) and the addition of a promoter (e.g., Ce, Mg) compounds were analysed.

CO_2 and CH_4 conversions close to thermodynamics were exhibited by most of the zeolite-based samples, with 10 wt% Ni displaying the best results for the monometallic series (60% CH_4 conversion and H_2/CO ratio ~1 at 600 ºC). In addition, the incorporation of Ce and Mg, the second requiring higher pre-reduction temperatures due to the formation of Ni-Mg mixed oxides, led to a improvement of the metallic dispersion, enhancing the performances (75% CH_4 conversion and H_2/CO ratio ~1 at 600 ºC in the best promoted catalyst) and hindering carbon deposition (<0.01 $g_{carbon}\ g_{cat}^{-1}$).

Acknowledgments
Authors thank to Fundação para a Ciência e Tecnologia for CQE and IMS funding (projects: UIDB/00100/2020, UIDP/00100/2020 and LA/P/0056/2020) and Carmen Bacariza' contract (2020.00030.CEECIND).

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Sustainable strategies for electrochemical CO_2 reduction

S. Messias[1], A. B. Paninho[1], A. V. M. Nunes[1], L. C. Branco[1], C.M. Rangel[2], A. S. Reis Machado[1,*]

[1] *LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal*
[2]*Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, 22 Lisboa, 1649-038, Portugal*
** ams.machado@fct.unl.pt*

Electrochemical CO_2 reduction is a CCU (Carbon Capture and Utilization) research technology that is being intensively investigated not only for obtaining chemical building block and fuels, but as an excellent future option to store energy from renewable sources, such as solar and wind energy, that are seasonal, intermittent, and geographical dependent. Another advantage of the used of CO_2 as a renewable carbon source in the electrochemical CO_2 reduction is the potential to close the anthropogenic carbon cycle. [1-3]

In previous works the development of an electrochemical process to produce syngas ($CO+H_2$) was reported [4,5]. The syngas produced by this green process can be used to synthetize an enormous variety of fuels and chemicals in a sustainable way.

This work reports the study of the influence of ionic liquid-based electrolytes in electrochemical CO_2 reduction and the development of new cathodes using aerogels as support. Ionic liquids are promising materials for the integration of CO_2 capture and electrochemical reduction, once they have interesting properties, such as negligible- volatility, high CO_2 solubility, high conductivity, and large electrochemical window. During this work, different families of ionic liquids have been tested and characterized by cyclic voltammetry and electrochemical impedance spectroscopy to evaluate their electrochemistry behavior for CO_2 electroreduction processes.

In the other approach, the aerogels are chosen to develop new cathodes due to their properties as open porous structures, large surface areas, high porosity, mesoporous pore size distribution, and low bulk density, which are desirable for catalytic applications. [6] Activity and faradaic efficiencies of the prepared catalytic cathodes are correlated with the morphologies of these materials determined by SEM and BET surface areas. In the two studies, the productivities of gaseous products resulting from the co-electrolysis of CO_2 and water together with their faradaic efficiencies have been also determined.

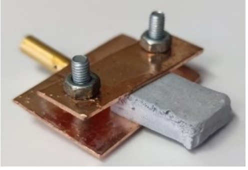

Fig.1. Cathode based methal aerogels

Acknowledgements

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Remarkable photocatalytic production of H_2O_2 using metal-free doped carbon nitride

André Torres-Pinto[1,2*], **Amanda Fujita**[1,2], **Cláudia G. Silva**[1,2], **Joaquim L. Faria**[1,2], **Adrián M.T. Silva**[1,2]

[1]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
andretp@fe.up.pt

Nowadays, the fabrication and application of sustainable nanomaterials have become one of the most highly explored topics in scientific research. In particular, the synthesis of photocatalytic materials is being more and more investigated, specifically graphitic carbon nitride (GCN), due to its excellent electronic and photo-responsive properties [1]. Typically, GCN materials present a relatively narrow band gap, allowing photo-excitation using visible light irradiation; however, they also show a fast rate of charge carrier recombination. In this way, there is an increasing concern to overcome this drawback by performing modifications of these materials, *e.g.*, doping, exfoliation or developing a heterostructure [1,2].

In this work, we developed a facile method for incorporating non-metal atoms (*e.g.*, P, B, O and S) into the GCN matrix by mixing selected molecules with urea and performing a rapid microwave-assisted thermal treatment. The synthesised materials were employed for the photocatalytic generation of H_2O_2 under aerated and neutral pH conditions in the presence of different proton donors, such as small-chain alcohols (methanol, ethanol and isopropanol) or recalcitrant pharmaceutical substances (venlafaxine, metoprolol and diclofenac).

The 1.0%wt. P-doped GCN material showed the highest H_2O_2 evolution rate (242.0 mmol g_{cat}^{-1} h^{-1}) among all tested materials, more than 13 times higher than bare GCN (17.8 mmol g_{cat}^{-1} h^{-1}). For instance, using methanol (10% *v/v*) as a sacrificial agent (Fig. 1), 1.2 mmol L^{-1} of H_2O_2 was yielded after 2 h of irradiation with bare GCN. In contrast, 1.6, 7.2, and 6.4 mmol L^{-1} of H_2O_2 were obtained for varying phosphorous percentages of 0.2%, 1.0% and 5.0%wt. P, respectively, proving that the incorporation of phosphorous in the GCN matrix allows for greater photocatalytic activity.

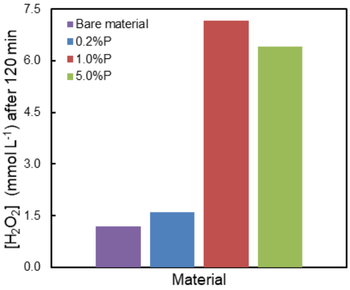

Fig.1. Photocatalytic H_2O_2 production using P-doped (0, 0.2, 1.0, 5.0% wt.) GCN in a 10% *v/v* methanol aqueous solution.

Acknowledgements
This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC), and by Project NORTE-01-0145-FEDER-000069 (Healthy Waters) supported by NORTE 2020, under the PORTUGAL 2020 Partnership Agreement, through ERDF. A.T-P. gratefully acknowledges FCT for his scholarship SFRH/BD/143487/2019.

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Highly efficient antimicrobial and self-cleaning cotton fabrics coated with graphitic carbon nitride

Maria A. Barros[1,2*], **Catarina L. Seabra**[3], **Maria J. Sampaio**[1,2], **Cláudia Nunes**[3], **Cláudia Silva**[1,2], **Salette Reis**[3], **Joaquim L. Faria**[1]

[1]Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[3]LAQV, REQUIMTE, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
*up201608044@fe.up.pt

Graphitic carbon nitride (GCN-T) is a photocatalyst widely used to degrade organic compounds, such as dyes, pesticides, insecticides, pharmaceutical compounds, and phenols [1]. In addition, under visible light irradiation, GCN-T catalyst can generate reactive species, including holes, superoxide radicals ($O_2^{\bullet -}$) and hydrogen peroxide (H_2O_2) that can interact with the membrane of bacteria, leading to cell death [2, 3]. Although the photocatalytic activity of coated fabrics with GCN-T materials combined with other catalysts has been studied for pollutant decomposition, its specific antimicrobial activity when immobilized has not been extensively reported. In this work, GCN-T was immobilized on cotton (CO) fabrics, and their antimicrobial and self-cleaning activity were examined under visible light. The antimicrobial activity was tested on commensal skin bacteria, *Staphylococcus spp.*, and on pathogenic bacteria, *Escherichia coli* and *Pseudomonas aeruginosa*. Under dark conditions, no antimicrobial effect was observed, but after 60 min of irradiation (Fig.1), the functionalized cotton (CO/GCN-T) revealed high antimicrobial activity against pathogenic bacteria.

Moreover, CO/GCN-T did not affect the growth of commensal skin bacteria, and its non-cytotoxic to skin cells (L929 fibroblasts and HaCaT keratinocytes) was proven. The self-cleaning properties of CO/GCN-T fabrics were confirmed for the degradation of RhB dye, as well as its reproducibility and reuse. These finds are particularly promising for application in healthcare centres, where the surfaces are continuously exposed to a large microbial community. Thus, the impregnation of GCN-T particles on surface subtracts can decrease or ideally eliminate the occurrence of harmful microorganisms.

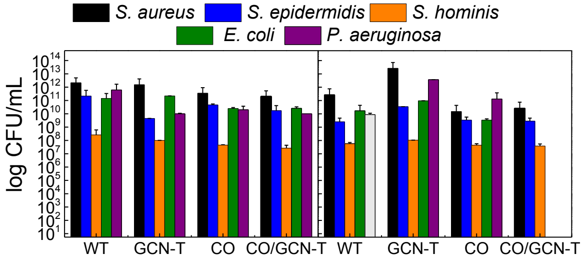

Fig.1. Logarithmic reduction of selected bacteria after direct contact with GCN-T powder, CO and CO/GCN-T in dark conditions and after 60 min of irradiation with visible light (LED λ_{max} = 420 nm, 160 W m^{-2}). WT means wild-type, untreated cells (control).

Acknowledgements
This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC), and ClimActiC Project - NORTE-01-0145-FEDER-000071 (PORTUGAL2020). The authors acknowledge the institution LAQV – Laboratório Associado para a Química Verde (project UIDB/50006/2020 | UIDP/50006/2020). MAB acknowledges the research grant from FCT (ref. SFRH/BD/145014/2019).

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Parabens removal using UiO-66-NH_2 under solar light

M. Peñas-Garzón[1,2,3,*], **M.J. Sampaio**[1,2], **Y.L. Wang**[3], **J. Bedia**[3], **J.J. Rodriguez**[3], **C. Belver**[3], **C.G. Silva**[1,2], **J.L. Faria**[1,2]

[1]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
[2]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
[3]Chemical Engineering Department, Universidad Autónoma de Madrid, Campus Cantoblanco, E-28049 Madrid, Spain
*manuelpgarzon@gmail.com

Parabens are compounds industrially used in the formulation of cosmetics and pharmaceuticals due to their antibacterial activity. They are considered endocrine-disrupting compounds whose bioaccumulation can represent a threat to ecosystems [1]. An exciting approach to eliminate these contaminants in water streams is heterogeneous photocatalysis. For that purpose, the use of metal-organic frameworks (MOFs) for photocatalytic environmental applications has received increasing attention nowadays due to the possible modulation of the MOF properties through the use of different metal precursors and organic linkers [2].

This research aims the evaluation of UiO-66-NH_2 (a Zr-based MOF) in the degradation of methylparaben (MP). Different water matrices were tested (Fig. 1a), achieving almost complete conversion after 1 h of solar irradiation in both distilled and river water samples. In contrast, the efficiency decreased in the secondary treatment effluent from a wastewater treatment plant (WWTP), probably due to the higher turbidity and organic/inorganic matter content. A continuous flow study proved the performance stability of the material upon 25 h on stream. The oxidation mechanism was proposed, where the highest contribution was ascribed to $O_2^{\bullet-}$ and h^+ (Fig. 1b), supported by electrochemical characterization. The photocatalytic performance of the MOF was also tested in removing other parabens, namely ethylparaben (EP) and propylparaben (PP), being observed that the efficiency depended on the alkyl side chain length of the compounds.

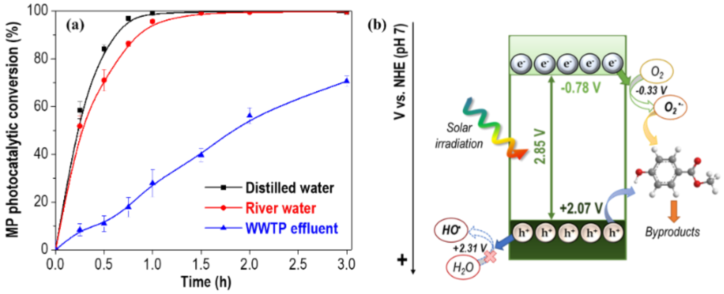

Fig.1. (a) Methylparaben conversion under solar light in different water matrices ($[MP]_0 = 3.3$ mg·L^{-1} (after adsorption); 0.75 g·L^{-1} of UiO-66-NH_2, 600 W·m^{-2} of solar irradiation); **(b)** Suggested MOF photocatalytic mechanism. (Adapted from [3]).

Acknowledgments

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C_3N_4-SiO_2 nanocomposites as visible light-active photocatalytic treatments for building materials

Manuel Luna[1,2,3*], **Cláudia G. Silva**[2,3], **María J. Mosquera**[1], **Joaquim L. Faria**[2,3]

[1]Nanomaterials Group TEP243, Faculty of Sciences, University of Cadiz, Campus Universitario Río San Pedro, 11510, Puerto Real, Spain
[2]LSRE–LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, Porto, 4200-465, Portugal
[3]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, Porto, 4200-465, Portugal
**manuel.luna@uca.es*

Nowadays, air pollution dramatically impacts the quality of life in big cities and industrial areas worldwide. The high concentration of pollutants is related to the proliferation of respiratory and cardiovascular diseases and a higher risk of cancer. In addition, other pollutants, typically associated with combustion processes, are deposited and accumulated on building facades, changing the aesthetic of historic buildings and promoting their deterioration. Photocatalysis is one alternative to mitigate these problems since it eliminates a wide range of pollutants by the action of light. In particular, the use of photoactive building materials could be of particular interest to achieve this purpose by reducing the pollutant levels in the air while protecting the buildings against fouling.

The use of TiO_2 for producing photocatalytic building materials is well-documented in the literature [1], and the use of silica as a binder allows to produce of photocatalytic TiO_2-SiO_2 coatings with self-cleaning and depolluting properties on existing buildings [2] and promotes the durability allowing an antifouling effect over a long period [3]. However, the TiO_2 absorption is limited to UV radiation, which is relatively scarce in sunlight. Graphitic carbon nitride (g-C_3N_4) is a promising visible light-active photocatalyst, but there are very few examples of their use on building materials.

The present work focuses on the use of g-C_3N_4 for producing photocatalytic treatments for building materials and evaluating its performance under visible light compared with TiO_2. g-C_3N_4 was integrated into synthesizing a SiO_2 sol applied by brush on cement mortar samples. The silica sol partially penetrated the pore structure substrates, and they gelled, *in situ*, producing a well-adhered g-C_3N_4-SiO_2 coating. The obtained nanocomposites and the treated samples were characterized to confirm the treatment's compatibility with the substrate. Finally, the photocatalytic properties of the treated samples were evaluated employing the degradation of methylene blue (MB) stains under 417 nm radiation (Fig. 1). About 53% of MB stain was eliminated in the g-C_3N_4-SiO_2 treated samples. In contrast, the degradation was only 16% for TiO_2-SiO_2 samples, confirming the higher effectiveness of the g-C_3N_4-SiO_2 treatment under visible light.

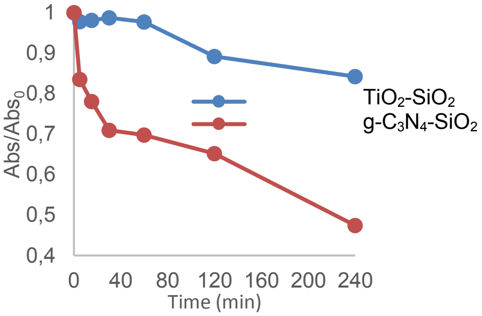

Fig1. Absorbance evolution of MB stains deposited on treated cement mortar samples.

Acknowledgments

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Ir(I)-catalyzed enantioselective hydrocarbonation of allenes: access to fused heterocycles bearing quaternary stereocenters

A. Rey,[1] A. Arribas,[1] J. L. Mascareñas,[1] F. López[1,2]

[1] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela (Spain),
[2] Misión Biológica de Galicia, Consejo Superior de Investigaciones Científicas (CSIC), 36080, Pontevedra (Spain).
alejandro.rey.lopez@rai.usc.es

Carbon-carbon bond formation are one of the most important features of organic chemistry. In this regard, classical cross coupling reactions are of a high importance due to how robust they are. However, as a consequence of the low atom economy and the huge waste generation that stoichiometric metallic reagents cause, these do not get along with the crucial shift towards a more environmentally friendly chemistry that nowaday's society is demanding. Furthermore, is to be highlighted the relevance that asymmetric synthesis has gained over the past decades, particularly for the pharma industry. This together with the need of more sustainable tools for the assembly of C-C bonds, puts asymmetric catalysis and C-H functionalization at the forefront of organic chemistry. [1]

In this context, we herein report an iridium(I)-catalyzed asymmetric hydrocarbonation of allenes, through a C-H activation/functionalization protocol. This methodology, which proceeds with full atom economy, provides access to a wide variety of cyclic scaffolds in good yields and high enantioselectivities. The use of allenes as hydrocarbonation partners complements our previous methodologies that make use of alkynes and alkenes, [2,3,4] while overcoming some of their drawbacks.

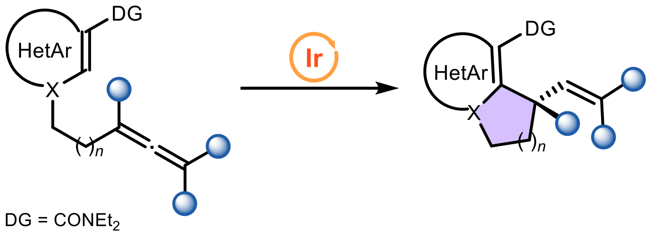

Fig.1. Iridium catalyzed Hydrocarbonation of allenes.

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Modulating the performance of electrocatalyst materials

Carlos Herreros-Lucas[1] , Melanie Guillén-Soler[1] , Glenn Murray[2] , José Manuel Vila-Fungueiriño[1] and María del Carmen Giménez-López[1,2]*

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS),
Universidade de Santiago de Compostela, 15782 Santiago de
Compostela, Spain.
[2]School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7
2RD, UK
**melanie.guillen@usc.es*

The large-scale hydrogen production, as a clean and renewable energy vector, depends greatly on the system used as electrocatalyst. This process is mainly restricted by the use of precious metal nanoparticles, which are expensive and scarce.[1] In this context, the electrolyte/electrode interface can play an important role to increase the lifespan of the electrocatalyst materials.[2]

In this work, we discuss different synthetic protocols and methodologies that can be implemented in order to increase the activity and durability of these precious metals for sustainable energy conversion processes, such as the hydrogen evolution reaction (HER). Controlling the nature of the support, as well as the surface nature of the electrocatalytic nanoparticles, is crucial to control their performance.

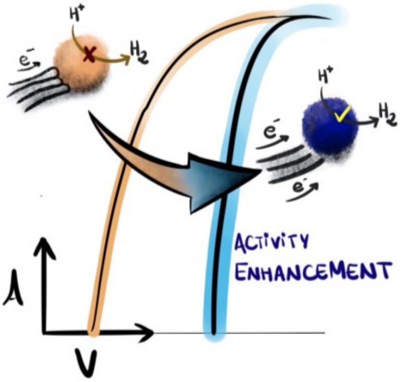

Fig.1. The tuneable performance in the HER activity of metal nanoparticles on the electrolyte/electrode interface.

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Sustainable synthetic catalytic processes for transformation of eugenol into potential fragrances

Vitaliy Masliy[*], **Madalena F. C. Silva, Fábio M. S. Rodrigues, Rui M. B. Carrilho, Mariette M. Pereira**

Coimbra Chemistry Center, Department of Chemistry, University of Coimbra, Rua Larga,
3004-535 Coimbra, Portugal
**vmasliy@qui.uc.pt*

During the 21st century, regulations over the chemical industry in the field of flavors and fragrances have significantly increased, as society interacts with these products in the daily life. As more and more compounds are banned every year from this market, there is a constant search for alternatives, especially those based on natural sources. [1] Among them, eugenol (4-Allyl-2-methoxyphenol) has gained significant attention in the development of fragrances, since it is an abundant, green and safe natural building block, with the advantage of having benign biological activity (antibacterial, anti-inflammatory, antioxidative). [2-3]

In this communication, we present our recent results regarding the implementation of catalytic processes for the structural modification of eugenol, namely acetylation, hydroformylation/acetalization, olefin epoxidation and carbon dioxide cycloadditions reactions, in order to obtain new potential fragrances. (Figure 1). The transposition of all these reactions from batch to continuous-flow systems, in order to achieve sustainable processes, with potential scale-up technology, will be described and discussed.

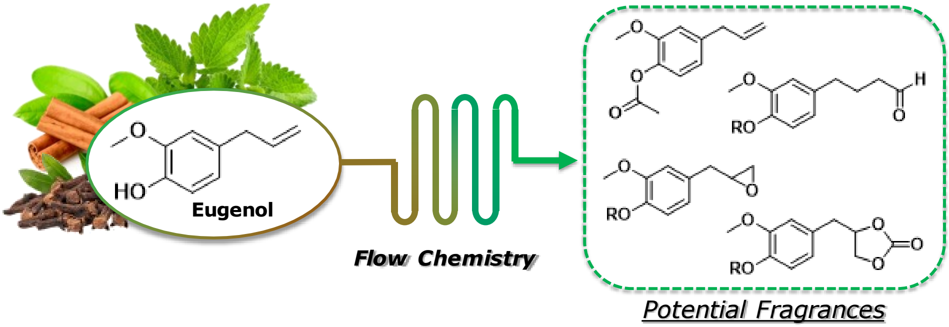

Figure.1. Flow chemistry processes for preparation of eugenol derivatives with potential fragrance application.

Acknowledgements
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Asymmetric Michael addition of nitromethane to chalcones mediated by chiral organocatalysts in ionic liquids

Sónia P. Lopes[1,*], Raquel G. Soengas[2], Humberto Rodríguez-Solla[2], Vera L.M. Silva[1], Artur M. S. Silva[1]

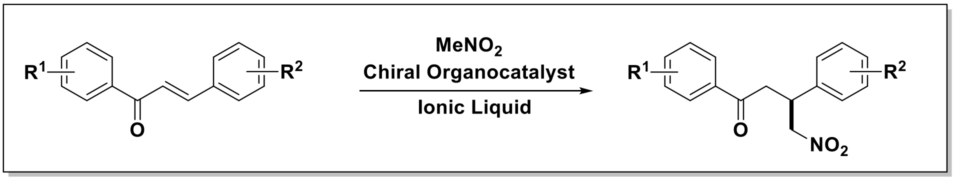
[1] LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2] Department of Organic and Inorganic Chemistry, University of Oviedo, 33006 Oviedo, Spain.
**sonialopes@ua.pt*

Asymmetric Michael addition mediated by chiral organocatalysts has been recognized as the most relevant and dynamic research area for the construction of chiral C-C bonds. Many addition products are important synthetic intermediates that can be transformed into a wide range of biologically active compounds [1]. Thus, this reaction stands of great relevance to the pharmaceutical industry for the synthesis of chiral drugs. However, over the years the use of drugs as racemates has been restricted, and therefore the development of efficient asymmetric reactions to obtain enantiomeric pure compounds has become a challenge in organic synthesis.

The economic and environmental concerns have been pressing the chemical community to search for more sustainable and greener synthetic methods. In this context, ionic liquids (ILs) have attracted considerable attention due to their unique and remarkable properties such as their non-flammability, non-volatility and negligible vapour pressure. Several studies have reported efficient asymmetric catalytic reactions using chiral catalysts performed in ILs [2]. The use of ILs showed an enhancement of catalyst stability, leading to excellent reactivities and enantioselectivities. Additionally, they allow an easy product recovery as well as the recyclability of the chiral catalyst/IL system [3].

The present work aimed to prove the potential of the combination of organocatalysts and ILs for efficient asymmetric Michael additions. For that, it was evaluated the addition of nitromethane to chalcones mediated by several chiral organocatalysts in ILs (Figure 1). Michael addition products were successfully synthesized with moderated to good yields (45–73%) but unfortunately they showed up as a racemic mixture. Further studies will be conducted to understand the mechanisms involved in this reaction and to improve the results obtained.

Fig. 1. Asymmetric Michael addition of nitromethane to chalcones mediated by chiral organocatalysts in ILs.



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ENSEÑANZA DE LA QUÍMICA

Utilización de metodologías activas para trabajar competencias transversales en asignaturas de Ciencias

Rodríguez-Cáceres, M.I.*[1], **Alexandre Franco, M.F.[1], Antón Martínez, M.[1], Botello Cambero, E.[1], Corchado Martín-Romo, J.C.[1], Cuerda Correa, E.M.[1], Cumplido Laso, G.[1], Durán Valle, C.J.[1], Espino Palma, J.[1], Fernández González, C.[1], Flores Regalado, A.[1], Garrido Álvarez, M., Gil Álvarez, M.V.[1], Luna Giles, F. [1], Martín Navarro, M.E.[1], Martínez Pizarro, M.[2], Martínez Vázquez, R.F.[1], Mora-Díez, N.M.[1], Obregón Muñoz, M.A.[1], Pardo Botello, M.R.[1], Parra Arévalo, M.I.[1], Sánchez Mendoza, M.L.[1], Sansón Martín, J.A.[1], Serrano Pérez, A.[1], Vaquero Martínez, J.[1], Viñuela Zahínos, E.[1], Zarza Belmonte, J.[1]**

[1]Facultad de Ciencias; [2]Centro Universitario de Mérida,
Universidad de Extremadura (España)
**maribelro@unex.es*

Desde 2015, profesores de Química, Física, Biología, Matemáticas y Estadística formamos un grupo que se consolidó en 2019 al constituir el Grupo Pluridisciplinar de Innovación Docente y Divulgación de Ciencias (GiDeCien). El objetivo del grupo fue trabajar competencias transversales con los estudiantes de Grado de la Facultad de Ciencias, principalmente las relacionadas con la expresión oral, ya que se venía observando la dificultad de los estudiantes en el momento de hacer la exposición y defensa de los Trabajos Fin de Grado (TFG). Para trabajar esta competencia, ofrecimos a los estudiantes de grado (unos 1500) un taller denominado “Hablar en público: prepárate para la defensa de tu TFG”, del cual van ya ocho ediciones. Este taller utiliza una metodología que combina, por un lado, sesiones de expertos en oratoria que proporcionan a los estudiantes pautas para una adecuada exposición oral, y los entrenan en el uso de las pausas, los silencios… y también en la comunicación no verbal. Y, por otro lado, los estudiantes deben seleccionar un artículo relacionado con su TFG y realizar una presentación oral y otra audiovisual, de tal modo que perfeccionan el uso de las TIC, así como la expresión oral y escrita.

En los últimos años y sobre todo desde el inicio de la pandemia causada por la COVID-19, nos hemos propuesto el reciclado tecnológico para aprender las herramientas de entornos virtuales. Para ello, durante el curso 2020-21 se trabajó sobre la elaboración de vídeos interactivos, virtualizando tanto contenidos prácticos como de informática. En el curso pasado, 2021-22, con el afán de la formación y adaptación de la docencia a los nuevos tiempos, trabajamos la metodología de Clase Invertida para favorecer un Aprendizaje inverso en el cual el alumno aprende a estudiar de una forma más personal y se focaliza en el desarrollo de la comprensión del estudiante más que en la memorización. En esta metodología, el uso de videos es una herramienta común y útil, ya que el estudiante puede visionar el material fuera del aula tantas veces como quiera, trabajando de manera individualizada y de acuerdo con sus necesidades. La puesta en práctica de esta metodología se llevó a cabo con un grupo de estudiantes del Grado en Física, del que un 30% no habían cursado Química en el bachillerato. Al finalizar el curso todos los estudiantes superaron la asignatura con mayor o menor dificultad y la mayoría mostró una valoración positiva de esta metodología, por la disponibilidad de vídeos en el Campus Virtual. En general, los vídeos los visualizaron cuando se propuso la actividad, pero también antes de los exámenes, por lo que les sirvió para repasar y facilitó su proceso de aprendizaje. En otros casos, se les proporcionó material impreso además de vídeos y al finalizar se les pasó un cuestionario del que se desprendió que la mayoría de los estudiantes lo valoraron positivamente.

La selección de herramientas pedagógicas que se adapten a las necesidades específicas de los estudiantes es de gran importancia ya que no todos los problemas admiten las mismas soluciones, de ahí que entre nuestros objetivos futuros pretendemos extender el uso de vídeos y clases inversas a más grados y asignaturas y también queremos desarrollar nuevas competencias transversales a través de la elaboración de material divulgativo, con lo que pretendemos completar la formación de nuestros estudiantes haciéndoles partícipes en actividades de divulgación.

Agradecimientos

Los autores agradecen la financiación de este trabajo al Vicerrectorado de Planificación Académica y al Servicio de Orientación y Formación Docente, por la ayuda concedida para la realización del proyecto de innovación docente: “Metodologías activas para trabajar competencias transversales”, así como a la ayuda concedida al grupo GiDeCien (https://www.unex.es/organizacion/servicios-universitarios/servicios/sofd/areas/ie/Catalogo_gids).

Tres tristes tigres comen mijo en un mijal

Ángel Vidal-Vidal*

Facultade de Ciencias (Dpto. de Química Física), Universidade de Santiago de Compostela, Campus de Lugo.
Avda. Alfonso X El Sabio s/n, 27002 Lugo, Galicia, Spain
**angel.vidal.vidal@usc.es*

Mediante la Resolución emitida el 3 de marzo de 2021, la Asamblea General de las Naciones Unidas declara el año 2022 como el Año Internacional del mijo. Los mijos son un grupo variado de cereales con semillas de pequeño tamaño, muy ricos en energía y que necesita muy poca cantidad de agua para crecer. Su cultivo se ve favorecido por la elevada productividad junto con la corta temporada de crecimiento incluso en condiciones de gran sequía y altas temperaturas. Por este motivo, el mijo es actualmente un cultivo muy importante en regiones semiáridas con climas tropicales pero puede convertirse en esencial en muchas partes del mundo en el futuro cercano debido a los efectos devastadores del cambio climático.

Estableciendo el año internacional del mijo se persiguen múltiples objetivos. Entre ellos, se busca reconocer la contribución del mijo al cultivo de alimentos nutritivos especialmente en entornos climáticos adversos, divulgar su contribución histórica a la seguridad alimentaria, y estimular el reconocimiento de los beneficios agrícolas y nutricionales de este cereal. Adicionalmente la Asamblea General de las Naciones Unidas exhorta a los estados miembros a adoptar medidas eficaces de cara a estimular y facilitar la producción y el consumo sostenible del mijo. Su gran diversidad genética, la capacidad de adaptación a múltiples entornos de producción y la ausencia de gluten son algunas características fundamentales de este alimento. Si a estas interesantes propiedades se le une que se es posible mantenerlo ensilado hasta 5 años sin que sufra modificaciones nutricionales significativas, se postula como un alimento fundamental a tener en cuenta para el futuro más inmediato.

Con el fin de contribuir al conocimiento y uso del mijo, desde las materias científicas de educación secundaria obligatoria y bachillerato es posible realizar diferentes actividades con este cereal.

En esta comunicación se muestra una propuesta didáctica experimental para la materia de física y química de 4º de ESO que tiene al mijo como protagonista fundamental. Para ello se parte de la pregunta, ¿Cómo de rentable es tener almacenado el mijo con respecto a otros cereales y legumbres? Para responder a esta pregunta es necesario razonar acerca de las variables que condicionan el almacenamiento como tamaño y forma del grano o la uniformidad del mismo etc y posteriormente, aplicar el método científico para comprobar o refutar las hipótesis establecidas. La clave para resolver esta pregunta reside en saber cuál es el volumen total del silo que está ocupado por aire y no por grano debido al empaquetamiento ineficaz de las distintas partículas. Para poder razonar qué especie posee el empaquetamiento más eficaz se determinan experimentalmente los valores de porosidad intersticial de los distintos alimentos.

Con unos pocos elementos como un picnómetro, una balanza, una probeta y un densímetro es posible trabajar conceptos tan variados como el método científico, estática de fluidos, principio de Arquímedes, magnitudes intensivas y extensivas o la diferencia entre densidad global, aparente y densidad real. También hay lugar a tratar las conversiones de unidades, el error sistemático y aleatorio y las fuerzas adhesivas y cohesivas entre otros.

Agradecimientos

Al profesor X. Proupín por la cesión del material y los fructíferos debates sobre el tema.

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Y nos dieron las diez y las once, las yodo, la una, las dos y las tres

Ángel Vidal-Vidal*

Facultade de Ciencias (Dpto. de Química Física), Universidade de Santiago de Compostela, Campus de Lugo. Avda. Alfonso X El Sabio s/n, 27002 Lugo, Galicia, Spain
**angel.vidal.vidal@usc.es*

La materia de física y química en las etapas escolares debe contribuir a que el alumnado entienda el funcionamiento del mundo que los rodea, analice los motivos por los que ocurren los principales fenómenos físicos y químicos de su entorno más cotidiano e interprete los mismos con base en las diferentes leyes y teorías científicas. Es importante no centrarse únicamente en aspectos macroscópicos observables, sino también intentar realizar una inmersión en el mundo microscópico, alcanzando de esta manera una verdadera comprensión del fenómeno estudiado. A medida que vamos profundizando en las causas, los conceptos se vuelven más abstractos y más desafiantes. Este hecho es una gran fuente de dificultades para el alumnado por lo que es preciso incorporar nuevas estrategias docentes para facilitar su comprensión.

Lograr el aprendizaje significativo de conceptos abstractos requiere que el alumno interactúe con el objeto de conocimiento, por ejemplo mediante trabajos prácticos. El acercamiento vivencial que los alumnos realizan mediante estas actividades experimentales no solo propicia que comprendan los conceptos, sino que también emitan hipótesis, interpreten fenómenos y se acerquen a la metodología y a los procedimientos propios del método científico y de la ciencia. Este trabajo experimental origina una gran cantidad de conflictos cognitivos y favorece el desarrollo de numerosas competencias.

Un ámbito que se presta en gran medida a la realización de trabajos prácticos para la comprensión de conceptos abstractos es la cinética química. Esta disciplina se ocupa de manera general de analizar la rapidez con la que acontece una reacción química además de comprender las variables que afectan (positiva o negativamente) a dicha reacción. El análisis de algunas de estas variables (principalmente a nivel cualitativo) se incorpora en el currículo de enseñanza secundaria y bachillerato.

En esta comunicación se presenta una reacción química muy visual y fácil de realizar con elementos cotidianos como medio para estudiar algunos de los principales factores que afectan a la velocidad de una reacción química. El sistema seleccionado es seguro y de bajo coste por lo que su uso se encuentra al alcance de cualquier centro de educación secundaria y bachillerato e incluso de la mayoría de los hogares. A lo largo de la propuesta, gracias a diferentes experimentos se analizan en detalle algunas variables que condicionan la velocidad de reacción a la vez que se introduce la interpretación microscópica. La dificultad y extensión de esta propuesta es fácilmente modulable por lo que se puede aplicar desde 3º de ESO hasta en una química general de primer curso de universidad. Viajando de lo cualitativo a lo cuantitativo se generan interesantes y variadas experiencias que permitirán a los alumnos lograr un aprendizaje significativo de la cinética química.

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QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Captura de CO_2 con carbones preparados a partir de serrín de pino (*Pinus radiata*)

C.H. Pimentel*, **L. Díaz-Fernández, D. Gómez-Díaz, M.S. Freire, J. González-Álvarez**

Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, España
**catarinahelena.dasilveira@rai.usc.es*

Los cambios climáticos asociados al aumento de emisiones de gases de efecto invernadero (GEI) son una de las mayores preocupaciones a nivel mundial. Entre los GEI, el CO_2 contribuye en más del 60% al calentamiento global debido a las enormes cantidades liberadas a la atmósfera [1]. Por este motivo se vuelve esencial el desarrollo de técnicas para su separación y almacenamiento. La técnica de adsorción es una de las más eficientes, pudiéndose aplicar de forma sostenible y con una buena relación coste-eficiencia. Por ello, interesa promover el uso de adsorbentes como los carbones activados, obtenidos de precursores renovables y económicos como es el caso de la biomasa [2]. En el presente trabajo se prepararon carbones a partir de serrín de pino (*Pinus radiata*) con el fin de estudiar su capacidad para la separación de CO_2 por adsorción.

Se prepararon y caracterizaron seis carbones: uno tras una etapa de carbonización a 600ºC (PSC), tres activados con KOH a diferentes temperaturas, 850 y 600ºC y dosis de agente activante,1:4 y 1:2 p/p (PSCA850-K-4, PSC600-K-4 y PSCA850-K-2) y otros dos activados con $ZnCl_2$ 1:4 p/p mediante un método de activación seca y otro húmeda (PSCA850-Z-D y PSCA850-Z-W, respectivamente). Los materiales se caracterizaron utilizando técnicas como microscopia electrónica de barrido (SEM) y la adsorción volumétrica de N_2 a -196ºC y CO_2 a 0ºC. Además, se determinaron las isotermas de adsorción de CO_2 y N_2 a diferentes temperaturas que se ajustaron a los modelos de Langmuir, Freundlich y Toth y se estudió la selectividad aparente CO_2/N_2.

Los carbones mostraron valores elevados del área superficial determinada con N_2 (entre 293 y 2865 m^2/g) y de la microporosidad (entre 68 y 91%) que favorece la adsorción de CO_2 [1]. Se observó que la adsorción de CO_2 disminuye con el aumento de la temperatura lo que sugiere que se trata de una adsorción de tipo físico [3]. El material que presentó mejores resultados con relación a la capacidad de adsorción de CO_2 fue el carbón activado con KOH en la proporción 1:4 (p/p) a 600ºC, con una capacidad de 5,79 mmol/g a 0ºC y 780 mmHg lo que se atribuye a su elevado porcentaje de microporosidad (89%). También presentó los valores más elevados de selectividad entre 19 y 21. En general, la isoterma de Toth fue la que mejor se ajustó a los datos experimentales.

Teniendo en cuenta los resultados obtenidos, los carbones derivados del serrín de pino se postulan como materiales prometedores para su aplicación en procesos de separación/purificación de corrientes gaseosas.

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Study and modeling of the equilibrium and dynamics of post-combustion CO_2 adsorption using carbon-based adsorbents

V. Rahimi[1,*] , **A. Ferreiro-Salgado**[1], **D. Gómez-Díaz**[1], **M.S. Freire**[1], **J. Gónzalez-Alvarez**[1]

[1] Department of Chemical Engineering, School of Engineering, Universidade de Santiago de Compostela Rúa Lope Gómez de Marzoa s/n. 15782, Santiago de Compostela, Spain

[*] *vahid.rahimi@rai.usc.es*

There has been an increase in global average surface temperature since pre-industrial times which is termed as global warming [1]. Climate change is the adverse effect of this warming, and it can disrupt not only the human beings lives but also of all the other living organisms. Greenhouse gases, particularly carbon dioxide (CO_2), are released in the environment mainly due to the combustion of fossil fuels, contributing to the global warming and climate change. Therefore, it is mandatory to implement technologies at large scale for CO_2 capture for use and storage in order to significantly reduce the greenhouse gas emissions in time and protect the environment [2].

The main challenges of post-combustion CO_2 capture, in which CO_2 is separated after the combustion of fossil fuels in large stationary sources, are the high flow rate of flue gases and the low partial pressure of CO_2, which reduces the separation potential and is also energy intensive. Adsorption is a separation technology with the potential to reduce the required energy for CO_2 capture and increase its recovery capacity in comparison to other separation techniques [3, 4]. The ideal post-combustion adsorbent needs to offer a series of characteristics: availability, CO_2 selectivity, sufficient adsorption capacity, a high stability (long life), ease of regeneration, and low cost. Carbon adsorbents fulfill all these requirements as they can be obtained at low cost from a renewable and globally available source such as biomass, they are selective towards CO_2, they can be easily regenerated, and unlike other physical adsorbents, such as zeolites or MOFs, they are hydrophobic and show high stability in wet conditions. In this work, a simulation process was applied to evaluate the performance of carbon-based adsorbents fabricated from olive stones (one carbonized at 600° C and other carbonized under the same conditions and activated at 850° C with a carbon/KOH ratio of 1:2 w/w) based on the CO_2 adsorption capacity under post-combustion conditions.

Firstly, after characterizing the carbons by a physical adsorption of N_2 at -196° C using a volumetric apparatus (Micromeritics ASAP 2020), regression analysis of the experimental data obtained for the adsorption isotherms of pure CO_2 and N_2 at 0° C, 25° C and 50° C between 0 and 1.1 bar was performed. For both carbons, comparing the adsorption isotherms of CO_2 and N_2 at different temperatures, it could be found that an increase in temperature diminished the amount of CO_2 and N_2 adsorbed. Likewise, the adsorption capacity decreased with decreasing pressure. The adsorption capacity of N_2 was significantly lower than that of CO_2. Then, as the ratio of the adsorption capacities for pure CO_2 and N_2 is usually taken as an indicative of the equilibrium selectivity, a selective CO_2 capture could be expected.

Then, binary dynamic adsorption simulations were carried out using a fixed bed adsorption model in Aspen Adsorption V10. CO_2/N_2 breakthrough curves were obtained by feeding a mixture of 14% CO_2 and 86% N_2 to the bed at 1.1 bar and 30° C. The results obtained from dynamic simulations demonstrated that the carbon-based adsorbents prepared can separate the CO_2 from a binary N_2/CO_2 stream at a CO_2 partial pressure representative of real post-combustion conditions, which showed a high CO_2 over N_2 selectivity. CO_2 is desorbed relatively easily, by simply purging the bed at 30° C, without the need for heating, which is interesting from the point of view of the energy consumption.

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Estudio físico-químico de sistemas de Triton X-102 + sales

Ana María Gayol[1,2,*], **Diego Gómez-Díaz**[3], **José Manuel Navaza**[3]

[1]Departamento de Física Aplicada, FA2, Universidad de Vigo, Lagoas-Marcosende s/n, 36310 Vigo. España.

[2]Universidad Francisco de Vitoria, Master de Prevención de Riesgos Laborales, Carretera Pozuelo a Majadahonda km 1,8, 28223 Pozuelo de Alarcón, España.

[3]Universidade de Santiago de Compostela, ETSE, Lope Gómez de Marzoa s/n, 15705 Santiago de Compostela.

**e-mail:anagayol@uvigo.es*

En este trabajo se desarrolla el estudio de dos sistemas de dos fases acuosas utilizando diferente tipo de sales, debido a su utilización en diversidad de campos, desde la alimentación, procesos de separación del etanol, industria cosmética, entre otros.

Se procede a estudiar el comportamiento de los sistemas binarios obtenidos a partir del polímero 20, Triton X-101 + agua + sal (Na_2SO_4 o K_2HPO_4) en función de la temperatura desde 288.15 K a 308.15 K y a presión atmosférica.

Las propiedades físicas [1] estudiadas son la densidad [1,3,5], el índice de refracción [1-4] y la velocidad del sonido en el laboratorio, en las condiciones ambientales que se mencionaron. Finalmente, en base a ellas se procede al cálculo, para la obtención de las propiedades derivadas que en este caso son: el volumen molar de exceso y la compresibilidad isentrópica también a presión atmosférica y en rango de temperatura 288.15-308.15 K.

La densidad y la velocidad del sonido fueron medidas en un densímetro tubo vibrante Anton Paar DMA 5000.

Se han estudiado los sistemas Triton X-102 + Na_2SO_4 + agua y Triton X-102 + K_2HPO_4 + agua. Se trata de una combinación de sistemas binarios ya que los sistemas polímero agua son completamente miscibles, mientras que sal + agua es parcialmente miscible. La concentración de saturación esta en torno al 25% en ambos casos.

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Viscosidad dinámica de sistemas binarios n-octano +1-alcohol

Ana María Gayol[1,2,*], **Santiago Castelo**[1], **Manuel M. Piñeiro**[1], **José Luis Legido**[1]

[1]Departamento de Física Aplicada, FA2, Universidad de Vigo, Lagoas-Marcosende s/n, 36310 Vigo. España.
[2]Universidad Francisco de Vitoria, Master de PRL, 28223 Pozuelo de Alarcón, España.
**e-mail:anagayol@uvigo.es*

Este trabajo se basa en la continuación de estados de propiedades termodinámicas como densidad, viscosidad y propiedades derivadas. El estudio se realiza en el rango de temperatura de 288.15 K a 308.15 K a presión atmosférica. Previamente se estudiaron diversos sistemas binarios [1-5]. En los últimos años se realizaron numerosos estudios sobre la viscosidad dinámica de mezclas de n-alcanos + 1-alcohol [1-6, 8-12]. Este trabajo realiza una comparación del comportamiento de la viscosidad y densidad con mezclas binarias n-octano + 1-alcohol.

La densidad se midió utilizando un densímetro de tubo vibratorio Anton Paar DMA 4500. Los detalles sobre el procedimiento experimental, la calibración y el control de temperatura se pueden encontrar en Lago et al [13]. Usando este método, la densidad se determina con una incertidumbre de 10^{-4} g cm^{-3} en todo el rango de temperatura. Las mediciones de viscosidad se realizaron con un viscosímetro Anton Paar AMV 200 conectado a un baño de circulación de fluidos PolyScience, que controla la temperatura con una incertidumbre de 10^{-2} K. Este dispositivo determina la viscosidad del fluido a través de la medición del tiempo dejando caer una bola de acero rodando. dentro de un capilar de vidrio lleno de muestra [14].

La desviación de la viscosidad dinámica de las mezclas binarias de n-octano + 1-alcohol disminuye al aumentar la concentración de 1-alcohol y la temperatura. Además, presenta una asimetría, encontrándose el mínimo en fracciones molares ricas en 1-alcohol. La desviación de la viscosidad presenta un valor mínimo para el 1-alcohol más largo. Se utilizó una ecuación tipo Redlich-Kister [7] para correlacionar las propiedades derivadas de las mezclas binarias que forman el sistema ternario, por el método de mínimos cuadrados no ponderados, el peso de todos los puntos experimentales es igual:

$$\delta Q_{ij} = x_i \cdot x_j \cdot \sum_{p=0}^{m} A_p \cdot \left(x_i - x_j\right)^p$$

En la ecuación, δQ significa el cambio de una magnitud Q ($\Delta\eta$, desviación de la viscosidad). Qi es la magnitud del disolvente puro, N es el número de componentes en las mezclas y xi es la fracción molar.

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Obtainment of different biosurfactant extracts from corn steep liquor depending on the extraction process

A. López-Prieto*, A. Martínez-Arcos, X. Vecino, J.M. Cruz, A.B. Moldes

CINTECX, Chemical Engineering Department, University of Vigo, 36310 Vigo, Spain

*alexlopez@uvigo.es

Biosurfactants are natural surface-active compounds produced by microorganisms with similar properties to chemical surfactants, though with the advantage of being more biocompatible and more biodegradable. An example of a source for the extraction of these compounds is corn steep liquor (CSL), an agro-industrial fermented stream where the biosurfactants are produced spontaneously [1]. To carry out the extraction of biosurfactants from CSL, different methods can be performed, such as: i) liquid-liquid (L-L) extraction or ii) solid-liquid (S-L) extraction. Each of these methods allow to obtain a biosurfactant extract with different properties, determining its final industrial application. On one side, L-L extraction processes with organic solvents, such as ethyl acetate, provide oily biosurfactant extracts; with a composition that includes lipopeptides, antioxidants, phospholipids and other bioactive compounds like organic acids; and are able to reduce the surface tension of water in more than 30 units with a critical micellar concentration (CMC) around 150-400 mg/L, depending on the grade of purity achieved and the organic solvent used [2,3]. On the other side, S-L extraction processes, in which buffer solutions (i.e. PBS) are used as extracting agents, provide cell-bound biosurfactant extracts adhered to the microbial biomass contained in CSL. These biosurfactant extracts are characterized by a lower content in fatty acids and a high content of amino acids, which confer them a white powder appearance, being able to reduce the surface tension of water up to 50-55 mN/m, similarly to those biosurfactants extracts produced by lactic acid bacteria though with CMC values [4]. In addition, the biosurfactant extract obtained from CSL with a S-L extraction process, contained gramicidin in its composition, which gives the extract antibiotic properties, opening the door to new applications [5].

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Biodiesel production from residual cooking oils and its purification by adsorption processes based on adsorbents of natural origin

Maria I. L. Garção[1,2,*], **Maria Carolina Sérgi Gomes**[3], **Ana Queiroz**[1,2], **António E. Ribeiro**[1,2], **Paulo Brito**[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Universidade Tecnológica Federal do Paraná, Jardim Paraíso, 86812-460, Apucarana, Brasil
**m.limagarcao@gmail.com*

Total global energy consumption has increased significantly in recent decades, and nowadays the main sources of world energy are oil, coal and natural gas. In addition to environmental concerns, the limited availability of fossil fuels has increased the interest in exploring alternative energy sources. In this quest, biofuel is a promising renewable energy source with low carbon emissions, also, it can be produced from a variety of resources, including waste cooking oil (WCO). Biodiesel is renewable, biodegradable, non-toxic, sulfur-free and free of aromatic carcinogens [1].

Biodiesel is produced by transesterification/esterification, a reaction that converts oil or free fatty acids into alkyl esters, also known as Fatty Acid Alkyl Esters (FAAE's). The properties of biodiesel depend on the raw materials used in its manufacture, and it should be similar to petroleum diesel to be used in engines without modification. All parameters are defined by standards, such as EN 14214-2008, which is the standard used in Europe [2]. To attend to all the requirements, the biodiesel must go through a purification process, which is important to remove impurities in the final product, such as excess alcohol, glycerin, etc. In this work, the chosen process for purifying the produced biodiesel is adsorption, the phenomenon in which solutes bind to solid surfaces. It is widely used in chemical and biochemical processes to recover or remove certain substances [3].

Several studies have been carried out on the purification of biodiesel by adsorption. Materials such as silicates, clays, polymers, among others. are widely used as adsorbents. Combined with the need to purify biodiesel and the proposal to reuse waste oil, cork residue is being investigated as a potential adsorbent because it is a porous material with a large surface area [4].

The first stage of the research was the optimization of biodiesel production. The effects of factors such as oil:alcohol molar ratio, catalyst load and reaction temperature on the transesterification of WCO samples with ethanol were investigated. Afterward, the study continues with the production of activated carbons from cork residue samples in order to investigate the removal efficiency of glycerol in different samples of crude ethyl biodiesel synthesized under the optimal conditions of oil alcohol ratio, catalyst loading and reaction temperature. Finally, the cleaned biodiesel is analyzed to verify if it meets the specifications of the EN 14214 standard. As part of the optimization of biodiesel production, preliminary studies have shown that the best FAAE's yield is achieved at 30°C, 1% w/w catalyst load and a 1:9 oil:alcohol molar ratio. Subsequently, a study covering the carbon materials synthesis and their respective characterization has been carried out.

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Study of biodiesel production from waste cooking oil by ethyl transesterification and its purification using adsorption processes

Gabriel L. Camilo[1,2,*], **Maria Carolina Sérgi Gomes**[3], **Ana Queiroz**[1,2], **António E. Ribeiro**[1,2], **Paulo Brito**[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Universidade Tecnológica Federal do Paraná, Jardim Paraíso, 86812-460, Apucarana, Brasil
**glaminocamilo@gmail.com*

In the year 2020, global biodiesel production reached 46.45 million tons, with biodiesel from waste cooking oils (WCO) constituting approximately 10% of this total, with Europe accounting for approximately 33% and Brazil 12% of global production [1]. The cost of conventional biodiesel production is higher than the production of diesel from petroleum, since it is produced mainly from high quality virgin oils, it is estimated that 70 to 80% of the total cost of biodiesel production is associated with the cost of the raw materials [2]. With this perspective, biodiesel production from WCO has become an economic opportunity and an environmental strategy to help address global renewable energy challenges and contribute to a sustainable society [3]. Oil with hours of frying at high temperatures results in the loss of its edible properties and nutritional value, the disposal of used cooking oil remains an issue due to its environmental and human health threats [4]. In this scenario, the collection and destination of these oils for the production of a value-added and environmentally friendly biofuel presents itself as an opportunity to be investigated. Adsorption and ion exchange are the most commonly used affinity separation processes in biodiesel purification worldwide, these methods are also known as dry washing methods. In these processes, an appropriate adsorbent is used to selectively remove certain impurities from the liquid phase onto its surface. Dry cleaning offers several advantages, including simple integration into an existing plant, shorter purification time, lower water consumption and lower effluent generation.

In this work, an optimization of the production of biodiesel from a WCO by the ethylic route is sought, through its characterization and purification by adsorption using natural adsorbents, focusing on the removal of glycerol. In a preliminary analysis, some required conditions for the production were found, such as: minimum catalyst load established at 0.9% (wt/wt), and better biodiesel yields obtained at lower temperatures. A response surface methodology was constructed using a Box-Behnken design with 3 parameters: alcohol/oil molar ratio, reaction temperature and catalyst load, and one response: biodiesel yield. The results indicate greater yields at lower temperatures and higher alcohol/oil molar ratios. In sequence, using olive stones as a natural carbon source, characterization of adsorbent materials based in the crude olive stone sample and in activated carbons produced from it by different chemical and physical activations were carried out, with the objective of selecting adsorbents for further tests of adsorption with the main goal of removing glycerol from the biodiesel produced.

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Identification of gramicidin in biosurfactant extract by ESI-MS: a preliminary study

Ksenia Lvova[1*], Andrea Martínez-Arcos[1], Alejandro López-Prieto[1], Xanel Vecino[1], B. Pérez-Cid[1,2], José Manuel Cruz[1], Ana Belén Moldes[1]

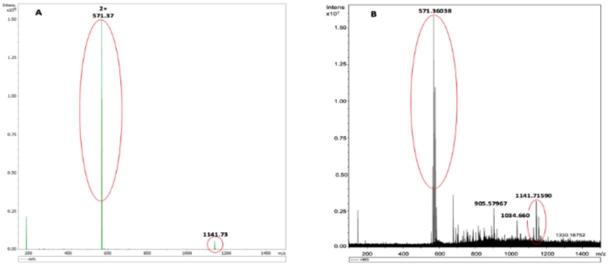
[1]Chemical Engineering Department, School of Industrial Engineering – CINTECX, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain
[2]Food and Analytical Chemistry Department, Faculty of Chemistry, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain
**kseniaaleksandrovna.lvova@uvigo.es*

Studies were conducted to obtain biosurfactant extract from *Aneurinibacillus aneurinilyticus,* a Bacillus strain that can grow spontaneously in corn steep liquor (CSL), and determine the presence of gramicidin in this extract. The identification of gramicidin is challenging but can be very useful, as it may reveal even low concentrations of antibiotic in a multicomponent system like CSL, a residual stream of corn industry. Some authors have showed that *Aneurinibacillus aneurinilyticus*, using synthetic medium, can produce a cell-bound biosurfactant extract containing Gramicidin [1, 2].

CSL with 50% solids was centrifuged and the precipitate containing the biomass was washed several times with water, every time discarding the supernatants. Subsequently, the precipitate was subjected to PBS extraction [3]. Then, an aqueous phase with biosurfactants, obtained after centrifugation process, was subjected to a dialysis step to eliminate salts. Finally, the resulting solution was lyophilized and analyzed by ESI-MS. Samples of the Gramicidin-biosurfactant extract were analyzed using Electrospray Ionization-Mass Spectrometry/Collision-Induced Dissociation (ESI-MS/MS/CID) with a Bruker FTMS APEXIII, Fremont CA. Figure 1 shows two signals (571 and 1141 *m/z*) in the biosurfactant extract obtained from CSL, that it is in consonance with the spectrum of commercial Gramicidin S. Additionally, other signals (905 and 1034 *m/z*) were detected in the biosurfactant extract, which corresponded to the lipopeptides produced by *Aneurinibacillus aneurinilyticus*.

In the current work, it was demonstrated that corn steep liquor, a by-product of corn milling industry, spontaneously fermented by *Aneurinibacillus,* could be a valid alternative source of Gramicidin, producing a biosurfactant extract with antimicrobial properties. However, further studies are needed to optimize the production and extraction conditions.

Fig.1. ESI-MS of commercial Gramicidin S (A) and cell-bound biosurfactant extract from CSL biomass (B)



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Antioxidant activity of biosurfactant extracts obtained from corn steep liquor

A. Martínez-Arcos*, **A. López-Prieto, X. Vecino, A.B. Moldes, J.M. Cruz**

CINTECX, Chemical Engineering Department, University of Vigo, 36310 Vigo, Spain
*****andrea.martinez.arcos@uvigo.es

In the last few years, many studies have been focused on bioactive compounds obtained from natural resources [1]. In this work, a multifunctional extract obtained from corn steep liquor (CSL), with demonstrated antimicrobial and surfactant properties, has been evaluated to determine its antioxidant properties [2]. The bioactive extract was obtained from CSL using organic solvents, such as ethyl acetate, subjected or not to hydrothermal treatment, following the protocol established by Rodriguez-López et al [2].
The antioxidant capacity was determined by the DPPH radical scavenging method described by Von Gadow et al [3]. Bioactive extracts from CSL showed antioxidant activities with an EC_{50} between 4.02-13.92 mg/mL, depending on the organic solvent used during extraction and the hydrothermal treatment. Compared to synthetic antioxidants (e.g. BHT with EC_{50} about 2.54 mg/mL) or other natural antioxidant extracts (e.g. chia seed oil with EC_{50} around 0.76 mg/mL), CSL extract presented a higher EC_{50} value; however, it is necessary to take into account that this extract not only possesses antioxidants but also other biocompounds with surfactant and antimicrobial activities, what makes the extract obtained in this work an interesting additive for food and cosmetic formulations in comparison with chemical based surfactants, antioxidants, or preservatives.

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Optimization of the hydrothermal extraction of antioxidants from *Opuntia ficus-indica*

Ricardo M. Ferreira[1]; Noelia Flórez-Fernández[2]; Jorge A. Saraiva[1]; Susana M. Cardoso[1]; M. Dolores Torres[2,*]; Herminia Domínguez[2]

[1]LAQV-REQUIMTE, Department of Chemistry, Campus Universitário de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Chemical Engineering Department, Universidad de Vigo (Campus Ourense), Edificio Politécnico. As Lagoas, 32004 Ourense, Spain
**matorres@uvigo.es*

In recent years, and due the increase concern of the consumer to the sustainability of industrial processes, the search of environmentally friendly alternatives to obtain compounds for different industrial sectors has grown exponentially. Therefore, new principles of biorefinery and circular bioeconomy in which the use of natural resources such as green solvents and waste biomass is prioritized are required [1]. In this work, *Opuntia ficus-indica* seed pomace, resulting from seed oil extraction, was selected due to its richness in phytochemical compounds and high antioxidant capacity. This residue was characterized regarding the fundamental chemical composition of the pomace used as raw material, as well as the main bioactive phytochemicals. The pomace samples were submitted to hydrothermal extraction (autohydrolysis), a green process using water under subcritical conditions for the solubilization of different compounds. Towards understand the impact of the application of this technique, a ratio of 1:8 (w:v) was fixed and different final heating temperatures up to 120 °C - 220 °C were applied [2]. The filtered extracts were analyzed by means of HPLC and HPSEC, to determine the monosaccharide profile and the molecular weight of the oligomers. Different spectrophotometric methods were used, Folin was applied for the determination of the total phenolic compounds (TPC) and TEAC, DPPH and FRAP were applied in de determination of the antioxidant capacity of the extracts. The results are presented in **Table 1**. In general, the increase in temperature was accompanied by the increase in phenolic compounds, with the exception of 180 °C where a slight decrease was observed. As expected for the antioxidant capacity of the liquid extracts, it can be observed that those obtained at 200 °C, had a higher antioxidant capacity when compared to those obtained at the other temperatures. Therefore, according to the phenolic content, a high temperature would be preferred. Since the proposed technology provides a variety of commercially valuable components, which could contribute to the integral use of this by-product following a biorefinery approach, further characterization of other fractions and components will be carried out.

Table 1. Total phenolic composition and antioxidant capacity given by the TEAC, DPPH and FRAP colorimetric methods of the different liquors obtained by autohydrolysis.

	Samples	TPC (g GAE/100 g)	TEAC (g GAE/100 g)	DPPH	FRAP (g GAE/100 g)
				EC_{50} (mg/mL)	
Autohydrolysis	120 °C	7.7 ± 0.3	23.5 ± 1.5	-	3.6 ± 0.11
	140 °C	7.9 ± 0.5	27.1 ± 2.1	4.13	5.4 ± 0.12
	160 °C	8.2 ± 0.1	30.7 ± 0.4	3.84	5.1 ± 0.05
	180 °C	6.9 ± 0.1	42.1 ± 2.2	2.84	5.8 ± 0.04
	200 °C	12.8 ± 0.5	68.5 ± 1.4	1.05	14.5 ± 0.61
	220 °C	13.7 ± 0.4	17.3 ± 0.6	1.14	14.0 ± 0.18

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Valorization of liquid and solid extracts from *Undaria pinnatifida* using microwave assisted extraction

J. Queffelec[1], N. Flórez-Fernández[1], H. Domínguez[1], M.D. Torres[1,*]

[1]CINBIO, Universidade de Vigo, Department of Chemical Engineering, campus Ourense, Edificio Politécnico, As Lagoas s/n, 32004 Ourense, Spain.
**e-mail del autor de contacto: matorres@uvigo.es*

Undaria pinnatifida, also known as wakame in Asia, is an invasive brown alga. It would therefore be interesting to find outlets for this biomass rich in bioactive compounds and polymers. Indeed, its pigments for example fucoxanthin, chlorophylls “a”, “c1” and “c2” as well as its polymers (alginate and fucoidan) have demonstrated antioxidant, antitumoral, anti-inflammatory and antiviral properties [1].

In this work, we performed microwave assisted extraction to recover and study the properties of both liquid and solid extracts, following the concept of biorefinery [2][3]. We assessed the influence of the microwave assisted extraction temperature, from 120°C to 220°C, on the bio properties of the liquid extracts and on the alginate recovery. The composition of the solid fraction in function of the extraction temperature was also determined.

While the highest antioxidant activity, polysaccharides, sulfate, phenolic compounds, and protein content were obtained at 200 or 220°C (Table 1), the highest mineral content of the solid extracts was obtained at the lowest extraction temperature. The 220°C liquid extracts have also demonstrated interesting cell growth inhibition on Human ovarian carcinoma and Human cervical cancer cell, with IC_{50} of 0.57 ± 0.01 mg/mL and 0.76 ± 0.03 mg/mL respectively.

Regarding polymers, FTIR and rheology analyses showed that the alginate extracted at 160°C has the structural and viscoelastic properties of the commercial one.

U. pinnatifida extracts could thus have interesting applications in food, cosmetics, or biomaterial engineering.

Table 1. Influence of the hydrothermal treatment temperature on TEAC, phenolic compounds, protein, and sulfate content of the liquid extracts.

Extraction temperature (°C)	120	140	160	180	200	220
TEAC (mg TROLOX eq/g extract)	2.88 ± 0.48	3.80 ± 0.64	7.37 ± 0.82	23.54 ± 3.07	47.84 ± 1.76	47.64 ± 8.48
Phenolic compounds (mg phloroglucinol/g extract)	2.07 ± 0.04	2.55 ± 0.02	4.00 ± 0.12	20.25 ± 0.67	36.85 ± 2.86	34.63 ± 0.96
Sulfate content (mg/g extract)	22.90 ± 3.12	21.98 ± 0.59	17.01± 0.91	18.05 ± 0.64	16.64 ± 0.41	52.49 ± 1.54
Protein content (mg BSA/g extract)	0.92 ± 0.06	2.08 ± 0.13	5.61 ± 0.92	6.21 ± 0.18	6.69 ± 0.42	6.30 ± 0.60

Agradecimientos

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Characterization of the Mediterranean green algae *Caulerpa prolifera* and investigation of its antioxidant capacity using green extraction assisted by microwaves

Sheyma Inoubli[1,2], Noelia Flórez-Fernández[1]; M. Dolores Torres[1]; Herminia Domínguez[1,*]

[1]CINBIO, Universidade de Vigo, Department of Chemical Engineering, Campus Ourense, Edificio Politécnico, As Lagoas s/n, 32004 Ourense, Spain.
[2]Laboratory of Aromatic and Medicinal Plants (LPAM), Faculty of sciences of Bizerte, Carthage University, Tunisia
**herminia@uvigo.es*

Marine macroalgae are considered a promising source of bioactive compounds with diversified structures and significant biological activities. Over the years, they have played an important role in a variety of industries, including food, pharmaceuticals, and cosmetics. Further, they have contributed to the discovery of new drugs [1, 2]. The present work is aimed to explore the nutritional composition regarding fatty acids, proteins, carbohydrates, and mineral content of the Tunisian green seaweed *Caulerpa prolifera* and to assess its antioxidant activity using Microwave-assisted-extraction (MAE) within the green processing concept. The antioxidant features of *Caulerpa sp* extracts were studied in several geographic areas, but only a few studies were conducted on Mediterranean regions. To the best of our knowledge, this is the first study that reports the characterization and antioxidant capacity of the Tunisian algae *C. prolifera*.

Lipid content was determined using a mixture of chloroform, and methanol (2:1 v/v) following the procedures described by Sato and Murata [3] with slight modification. Fatty acids were analyzed with Gas chromatography-mass spectrometry (GC-MS) and carbohydrates by High performance liquid chromatography (HPLC). Mineral content was measured by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES). A microwave-assisted extraction method (Anton Paar Monowave, Power 850, stirrer speed 850 rpm) has been performed using water as a green solvent. In order, to select the optimum extraction conditions, different temperature (120, 150, 180, 210 °C), and time (3, 6, 9, 12 min) conditions were studied. The antioxidant activity was measured with the DPPH (2,2-diphenyl 1-picrylhydracyl), Trolox Equivalent Antioxidant Capacity (TEAC), and FRAP assays, and the phenolic content of each extract was also evaluated.

The moisture content of the lyophilized sample was around 4.98% w.b. Carbohydrates accounted for 45.16%, protein rate was about 20.6%, ash was around 10.56% and crude lipid was about 1.6%, all in dry basis. Analysis of the lipid composition revealed that 11 fatty acids were detected in *C. prolifera*. The proportion of palmitic acid (16:0) as the main component was about 48% of the total fatty acid content in accordance to green seaweed *Caulerpa racemosa* var pelata [4], and *Ulva rigida* [5]. Moreover, linolelaidic acid and methyl linoleate as polyunsaturated fatty acids were also abundant with a ratio of 20%, followed by linolenic acid (6.6%). Analysis of mineral content (mg/kg) of *C. prolifera* indicated that calcium content (163.29) being the highest among the macro elements, followed by sodium (30.92), magnesium (28.83), potassium (9.43) and phosphorus (8.13). The most abundant microelements (mg/kg) revealed were iron (30.66). MAE outcomes showed a significant antioxidant activity of FRAP, TEAC and DPPH at 210°C at different tested times. Moreover, assays indicated high amounts of polyphenol that goes from 2.06 g/100 g at 120 °C to 11.68 g/100g at 210 °C (t = 12 min). Overall, the results of this study could provide valuable information for further investigation of the bioactive compounds of *Caulerpa sp*.

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Modeling and simulation of biomass pyrolysis processes

Pedro Maldonado[1,2*], Giane G. Lenzi[3], Helder T. Gomes[1,2] and Paulo Brito[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] Departamento de Engenharia Química, Universidade Tecnológica Federal do Paraná, Ponta Grossa, Paraná 84016-210, Brazil
**maldonado.pe@hotmail.com*

Pyrolysis is a thermochemical process where organic matter is decomposed into gaseous products, oils constituted by tars, and non-volatilized residual char, through the elevation of the system temperature (400-800°C), in the absence of oxygen. This process can be modeled and simulated for deeper analysis and optimization. However, since the process is clearly influenced by a high number of operational parameters such as temperature, pressure and dozens of simultaneous parallel reactions, its simulation becomes significantly complex. Thus, the aim of this work is the modeling of a more robust pyrolysis process, considering more components present in tar composition, as well as the evaluation of pyrolysis products distribution under different pyrolysis temperatures: 400, 500 and 600°C. Hence, a model was developed based on second-order equations [1], using pyrolysis temperature as the main variable, achieving as result the yield of three macro components: gases, tar and residual char. The gas fraction is composed by: carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2); tar fraction is constituted by: benzene (C_6H_6), toluene (C_7H_8) and naphthalene ($C_{10}H_8$), and the residual char is accompanied by ash in its composition. Simulation was implemented using biomass data based on the composition of olive residues applying the chemical process simulation software UniSim Design. The modeling first step is biomass decomposition in a conversion reactor, applying the yields obtained using the previous equations, while the second step is the decomposition of residual char in a yield reactor, resulting in the elemental constituents: carbon ($C_{(s)}$), hydrogen gas (H_2), oxygen gas (O_2), nitrogen gas (N_2), solid sulfur ($S_{(s)}$), and ash.
It is possible to note that the pyrolysis model results (see Table 1), implemented with the Software UniSim Design, show, in general, compatibility with the results available in the literature [2, 3]. The model reveals low sensitivity for the yield results, when using different sources of biomass with similar compositions, possibly due to the use of the temperature as the main variable.

Table 1. Component mass and molar fraction after Pyrolysis, under different pyrolysis temperatures.

Component (%)	**400°C**		**500°C**		**600°C**	
	Mole	Mass	Mole	Mass	Mole	Mass
C_6H_7	2.09	8.14	1.96	8.09	1.50	7.39
C_6H_6	7.38	24.43	6.95	24.28	5.32	22.17
$C_{10}H_8$	1.50	8.14	1.41	8.09	1.08	7.39
$C_{(s)}$	37.13	18.90	30.39	16.32	22.50	14.41
CO	8.35	9.92	9.89	12.39	9.53	14.23
CO_2	8.85	16.50	8.61	16.94	7.74	18.16
H_2	24.89	2.12	31.61	2.84	43.39	4.67
CH_4	0.08	0.06	1.20	0.86	3.03	2.59

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NANOQUÍMICA Y NANOTECNOLOGÍA

Size and coating-dependent toxicity of silver nanoparticles to human monocytes and macrophages

Adelaide Sousa[1,*], Ana T. Rufino[1], Ana Lei[1], Félix Carvalho[2], Eduarda Fernandes[1], Marisa Freitas[1]

[1] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal.
[2] UCIBIO, REQUIMTE, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal.
**adelaidetsousa@gmail.com*

Silver nanoparticles (AgNP) are considered the most marketed nanomaterials worldwide, due to their antimicrobial and preservative properties, being applied in diverse sectors, from medicine to the food industry [1-2]. Their increasing use in our daily life raises concerns about the putative impact of AgNP on human health [3].

AgNP can enter the human body through many pathways, affecting the viability and activity of the immune system "guard cells" and ultimately contributing to the onset and development of an inflammatory response. Monocytes and macrophages play a pivotal role in our defense system, but the interaction of AgNP with these cells is still not clear [3].

Therefore, the main objective of this work was to evaluate the cytotoxic and pro-inflammatory effects of AgNP with three different sizes (5, 10 and 50 nm) and two different coating agents, PVP and citrate, in human monocytes isolated from human blood and human macrophages derived from a monocytic cell line (THP-1). To achieve this main goal, the effects of AgNP on cell viability, mitochondrial membrane potential, and cytokines release, were evaluated.

The results revealed that the AgNP were able to interact with both human cellular models, but human monocytes seemed to be more sensitive to AgNP exposure than human macrophages. It was observed that the initiation of an inflammatory response by AgNP in these cells was mainly associated with the disruption of $\Delta\psi m$ and the release of pro-inflammatory cytokines, culminating in the decrease of their viability. Concerning the influence of the physicochemical properties on the toxicity of AgNP, it was shown that the smaller PVP-coated AgNP were more harmful in both human cellular models. The findings of the present study provide new insights into the interaction of AgNP with the cells of the immune system.

Considering the increased daily use of AgNP, it is imperative to conduct further research on mechanistic pathways leading to AgNP-induced pro-inflammatory effects in living organisms.

Agradecimientos

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NN02

Electroactive porous frameworks based on redox-active organic building blocks for electronics applications

Manuel Souto[1,*]

[1]Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
*Manuel.souto@ua.pt

Besides their inherent porosity, Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) may also incorporate tuneable physical (electrical, optical and magnetic) properties which strongly depend on the selected building blocks, becoming very attractive for their implementation as integral components in electronic devices.[1] In recent years, electroactive organic molecules have emerged as promising building blocks for the design and construction of crystalline porous frameworks such as MOFs or COFs for different applications in electronics (Figure 1).[2] In the first part of the presentation, I will show the electrical conductivity enhancement of an iodine-doped perylene-based MOF by using two-probe single-crystal devices [3]. This conductivity enhancement is ascribed to the partial oxidation of the perylene ligands, as witnessed by spectroscopic studies and supported by theoretical calculations. In the second part, I will present a new family of electroactive tetrathiafulvalene (TTF)-based COFs using different extended conjugated linkages to study the influence of the spacer between the TTF moieties on the electrical conductivity. Combining the intrinsic porosity of COFs and electrical conductivity may give rise to multiple applications such as (opto)electronics and energy storage [4].

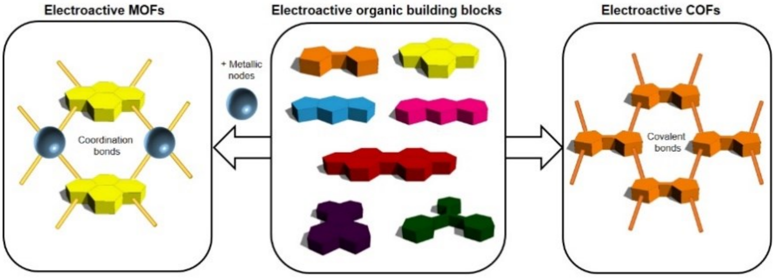

Figure 1. Schematic representation of the construction of metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) based on electroactive organic building blocks.

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New electrodes based on redox-active porous materials towards more efficient batteries

Raquel Dantas[1,*], **Manuel Souto**[1]

[1] Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal

**raqueldantas@ua.pt*

Today the energy sector is still the main contributor towards global warming, raising the urgency for a faster transition from fossil fuels to cleaner energy sources. Due to the renewable's intermittent availability problem, there is an increased need for better, safer, and more sustainable energy storage solutions.[1] This communication focuses on the use of Covalent Organic Frameworks (COFs), a type of organic polymer, as electrode materials for lithium-ion batteries.[2] First, the focus is centered on the synthesis and characterization of redox-active COFs, as well as the design of new COFs with expected increased conductivity.[3] Afterwards, the synthesized materials were used as electrodes in coin-cell type lithium batteries.[4] For that purpose, the electrode preparation process was optimized, and the batteries were manufactured and tested. Thus, uncovering relations between covalent organic frameworks and their application as electrode materials for energy storage devices.

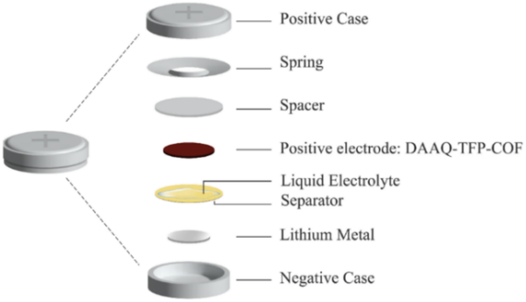

Fig.1. Schematic representation of the electrochemical half-cell assembly.

Agradecimientos

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Optimization of one-pot microwave synthesis of multicolored carbon dots

Ana L. Silva[1*], Catarina S. M. Martins[1,2], Marcela A. Segundo[1], João A. V. Prior[1]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy of the University of Porto, Porto, Portugal
[2]International Iberian Nanotechnology Laboratory, Braga, Portugal
**up202102798@ff.up.pt*

Carbon dots (CDs) are among one of the many carbon-based materials that have been target of research within the nanotechnology field for the better part of the twenty-first century. These fluorescent nanoparticles exhibit interesting physicochemical and optical properties, facile preparation, low cost, and high stability [1]. With sizes below 10 nm, they are composed of an inner graphene core and an outer surface rich in functional chemical groups [2]. Due to their structure and dimension, they can emit energy in the form of light with a high quantum yield (QY) and in a stable manner, when appropriately irradiated. Besides, their low toxicity and high biocompatibility make them ideal for applications in many biologically relevant fields like biosensing and bioimaging [3]. Like many nanoparticles, synthesis of CDs can be achieved through both ‘top-down’ and ‘bottom-up’ strategies. The latter methods are more commonly used, since they present some benefits, usually being less complicated and time consuming, more environmentally friendly, and easier to allow surface modifications [4]. It is therefore of high interest to control CDs fluorescence color by modelling their emission wavelength, a process that, although somewhat explored in the literature, is still difficult to attain, especially so using a fixed set of precursors and a hydrothermal approach.

In this work, we thoroughly exploited a hydrothermal one-pot microwave assisted green synthesis of CDs, using citric acid and o-phenylenediamine (oPD) as precursors. Aiming at the full control of the fluorescence emission wavelength (λ_{max}), while at the same time assuring the maximization of the QY, the synthesis variables of reaction time, temperature, pH and o-phenylenediamine/citric acid molar ratio, were studied by a design of experiments (DoE) approach. Monitorization of the as-synthetized nanoparticles was achieved by UV-Vis spectrophotometry, fluorometry and FTIR analyses. Relative fluorescence QY values were calculated using quinine sulphate or rhodamine 6G as the standard references, chosen in accordance with the emission wavelength range of the studied nanoparticles.

The resulting CDs reached different fluorescence emission regions, from blue to orange, depending on the set of synthesis conditions. Preliminary assays showed a significant influence of the reaction pH value, on the role that each studied synthesis’ variable, as well as their interactions, plays in defining both λ_{max} and QY. The experimental results revealed that performing the synthesis at different pH values will result in unique and specific influences of time and temperature on the studied benchmarks of λ_{max} and QY. Additionally, chemical ratios seemed to mostly influence the QY, with higher quantities of oPD increasing the registered values, seemingly without major shifts in the emission wavelength. The obtained results were used to establish a mathematical model to allow prediction of CDs’ optical properties by tuning the aforementioned synthesis parameters.

Future work will look to broaden the emission wavelength regions and further optimize the QY values for each color region.

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WO_3_naphthopyran hybrid nanomaterials: the new frontier to accomplish enhanced light-responsive textiles

<u>Marlene L. Pacheco</u>[1,*], Tânia V. Pinto[1], Céu M. Sousa[2], Alexandra Guedes[3], Paulo J. Coelho[2], Cristina Freire[1], Clara Pereira[1]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007, Porto, Portugal
[2]Departamento de Química e CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
[3]Instituto de Ciências da Terra e Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
** e-mail: up201811988@edu.fc.up.pt*

Nowadays, the exploration of light-responsive textiles for applications in camouflage, anti-counterfeiting, UV protection, and fashion is increasing. Hybrid photochromic nanomaterials based on the coupling of photoswichable inorganic (*e.g.*, WO_3, MoO_3) and organic compounds (*e.g.*, naphtopyrans, spiropyrans) are promising for the development of advanced light-responsive textiles since they present synergistic properties, enabling a fast response to sunlight/UV radiation, high color reversibility, and endurance to high temperatures used in the textile industry.[1,2] In this work, several photochromic inorganic-organic hybrid nanomaterials were produced through the functionalization of WO_3 with different naphthopyrans (NTPs) by two synthetic pathways: covalent *post-grafting* and *in situ* immobilization. The hybrid nanomaterials were incorporated onto cotton fabrics by screen-printing to produce tailor-made photoresponsive textiles (Figure 1).

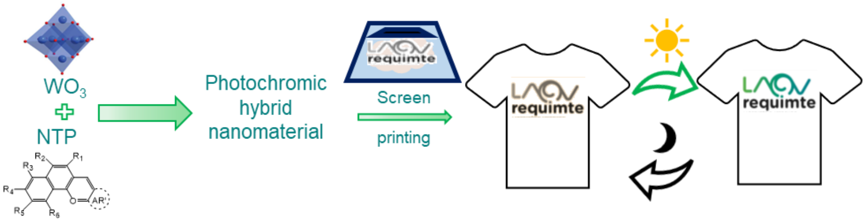

Figure 1. General scheme of the production of photochromic textiles.

The different pathways to immobilize the NPT (N1) onto WO_3 resulted in smart materials and textiles with distinct photochromic properties, namely the initial and final colors, the total color difference (ΔE) and the kinetics of coloration/bleaching. The *in situ* immobilization of N1 during the fabrication of WO_3 led to the hybrid with the best photochromic response (WO_3N1sil_*in situ*), which reached $\Delta E = 32$ after 30 min of UV light irradiation (also changing color under sunlight). More remarkably, the corresponding photochromic textile only took 2 min to change color under UV (also changing color under sunlight), and 6 h to reach 80% of the bleaching in the dark (Figure 2). The change of the type of grafted N1 modified the initial/final color of the hybrid but did not affect its photochromic behavior.

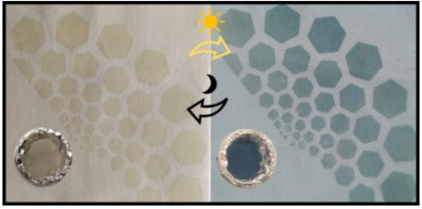

Figure 2. Photochromic WO_3N1sil_*in situ* material and respective smart cotton textile.

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NN06

Casein Micelles: Optimizing Encapsulation Towards Polyphenols Delivery

Maria Soares Macedo[1,2,*], Filipa A. Soares[1,2], Salette Reis[1], Cláudia Nunes[1,2]

[1]LAQV, REQUIMTE Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal
[2]ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Porto, Portugal
**mariasoaresmacedo@gmail.com*

In recent years there has been a growing interest regarding the effect of polyphenols, such as epigallocatechin-3-gallate (EGCG) and resveratrol (Resv) in the regulation of hypertension [1]. These bioactive molecules are highly susceptible to degradation under adverse conditions and are often associated with poor solubility, low stabilities, and low bioavailability [2]. Owing to the role that bioactive molecules can play in disease prevention, new methodologies such as nanoencapsulation have emerged to protect the molecules and enhance their biological activity [3]. Milk proteins are natural carriers that can be used for encapsulation and delivery of bioactive compounds in food, cosmetics and pharmaceuticals. In particular, caseins are used for the stabilization of emulsions and encapsulation of compounds due to their textural, flavour and functional characteristics [4].

Thus, this work aimed to encapsulate EGCG and Resv in natural casein micelles (CM) of bovine milk. Several conditions were investigated in the optimization of the protocol to extract casein from milk and encapsulate the bioactives in CM. Casein was extracted from skimmed milk through isoelectric precipitation by adding acetic acid in a ratio 1:100 (v/v). Nanoencapsulation of EGCG and Resv was achieved by resuspending lyophilized casein (1% w/v) in EGCG or Resv stock solutions (100 µM in PBS pH 6.8), under overnight magnetic agitation. The use of ultrasonication was then tested in the suspensions. The results proved that sonication of CM for 2 minutes A= 50% is an efficient way to control micelle size and increase its stability. Moreover, EGCG and Resv were encapsulated in CM with high encapsulation efficiencies of 92% and 70%, respectively. The binding of EGCG and Resv to CM was assessed by quenching the intrinsic fluorescence of casein. Incorporation of these compounds in CM caused a high quenching, which indicates the strong binding of the ligands to the protein. Hence, CM can bind both hydrophilic and lipophilic nutraceuticals.

Table 1. Casein micelle size distribution and encapsulation efficiency of EGCG and Resv.

Sample	Sonication	Mean size (nm)	PDI	Encapsulation Efficiency (%)
CM - Control	Non-sonicated	305 ± 69	0.341 ± 0.037	-
CM - EGCG		253 ± 74	0.292 ± 0.047	92 ± 9%
CM - Resv		255 ± 49	0.301 ± 0.054	69 ± 5%
CM - Control	2 minutes	169 ± 7	0.237 ± 0.011	-
CM - EGCG		172 ± 15	0.254 ± 0.022	91 ± 5%
CM - Resv		205 ± 28	0.247 ± 0.011	70 ± 5%

Acknowledgements

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Synthesis of TGA-capped CdTe quantum dots with controllable fluorescence wavelength

Catarina S. M. Martins[1,2*], Ana L. Silva[2], Alec P. LaGrow[1], Luís Pleno de Gouveia[3], João A. V. Prior[2]

[1]International Iberian Nanotechnology Laboratory, Braga, Portugal
[2]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy of the University of Porto, Porto, Portugal
[3]Pharmacological and Regulatory Sciences Group (PharmaRegSci), Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia da Universidade de Lisboa, Lisbon, Portugal
**up201304479@edu.ff.up.pt*

Quantum dots (QDs) are semiconductor materials, with a size range between 1–10 nm, that exhibit unique size-dependent physical and chemical properties [1]. Due to these excellent properties, in the last decades, their use has grown in several areas, namely in medical imaging and biosensing [2,3].

Most of the previous studies on the synthesis' optimization of thioglycolic acid (TGA)-capped cadmium and tellurium (CdTe) QDs do not include a mathematical tool to predict the maximum fluorescence emission wavelength (λ_{max}) control, nor does the synthesis follows a simple open-air procedure. The control of λ_{max} is the primary parameter for several applications of CdTe QDs, namely those dependent on the fluorescent optical properties. Therefore, by using a microwave-based straightforward aqueous synthesis of TGA-CdTe QDs, in atmospheric conditions, the influence of reaction time, temperature, Te:Cd and TGA:Cd molar ratios, in λ_{max} was studied following a chemometric Design of Experiments (DoE) approach.

The produced nanomaterials were characterized by UV-Vis and fluorescence spectroscopies. Moreover, Fourier-transform infrared spectroscopy and transmission electron microscopy were conducted for the syntheses corresponding to the DoE central points. Stable QDs with fluorescence ranging from green to red (527.6 nm to 629.2 nm, Figure 1) were obtained. Additionally, a statistical analysis of the same results revealed that the variables reaction time and temperature were the most significant factors influencing the obtained λ_{max}. Following, the chemical variables were fixed (TGA:Cd and Te:Cd molar ratios at 0.83 and 0.15, respectively) in order to fine-tuning reaction temperature and time, which were more significant. A mathematical model, with a predictive coefficient (Q^2) of 97,7%, was established capable of predicting the experimental conditions to synthesize TGA-CdTe QDs at a pre-chosen λ_{max}. This model was accurate in concern to the pre-defined λ_{max}, as confirmed in syntheses using the predicted conditions provided by the model.

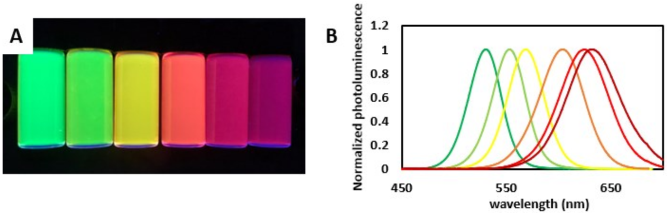

Fig.1. As-synthesized TGA-CdTe QDs: A – Representative photograph of the fluorescent colors range; B – Normalized fluorescence spectra.

Funding

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Magnetic nanoparticles for removing rare earth elements from water

<u>Daniela S. Tavares</u>[1,*], Raquel Fernandes[1], João Pinto[1], Bruno Henriques[1], Daniela Branco[1], Lina Carvalho[2], Tito Trindade[3], Eduarda Pereira[1,2]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[2]LCA, Department of Chemistry, University of Aveiro, Aveiro, Portugal
[3]CICECO, Department of Chemistry, University of Aveiro, Portugal
**danielatavares@ua.pt*

Rare earth elements (REE) are essential in a number of current technologies including electronic and optical device manufacturing, among many other processes [1]. At the end of their lifetime, electric and electronic products are often discarded without treatment leading to increased contamination in aquatic systems [2,3]. Efficient removal of REE from water bodies is not only a necessity for human and environmental well-being but it is also a strategy to reclaim critical elements that originate in electronic wastes. In the global scenario, natural REE resources are limited and secondary REE bearing sources are needed. REE recovered from contaminated waters can therefore be a promising alternative source, enhancing recycling rates and elements reuse. Conventional water treatment technologies are unsuitable for the effective removal of these elements at low concentrations and therefore advanced treatments are required. Sorption is one of the most efficient water treatment techniques due to its simple setup and operation [4]. The efficiency of the sorption process is mainly influenced by the properties of the sorbent and a variety of sorbents have been used. The use of nanomaterials in water treatment technology has attracted growing interest as sorbents because these materials can be designed with specific properties, and their small size confers a large specific surface area to capture elements present in water [5]. This work reports the application of spinel type ferrite nanoparticles - $MnFe_2O_4$, to removal and recovery of REE from contaminated water, thereby promoting the recycling of the elements. The influence of sorption parameters such as sorbent dose, time, temperature, and initial metal concentration on the sorption capacity of the materials was investigated. The sorbent (less than 200 mg/L) was able to sorb 100 % of a REE mixture consisting of La, Ce, Gd, Nd, Pr, Eu, Dy, Tb and Y in just 6 hours. Preliminary studies indicate that REE can be effectively recovered after sorption. In addition, magnetic nanosorbents composed of ferrites show an additional advantage, as they can be easily separated from the aqueous solution by applying an external magnetic field, thus allowing the reclaim of the REE.

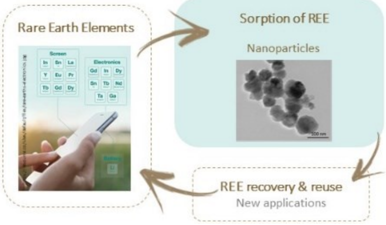

Fig.1. Removal and recovery of REE by nanoparticles for new applications

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Formulation of polymeric nanoparticles using a membrane fraction extract obtained by subcritical water extraction from *Laminaria ochroleuca* brown seaweed

Flórez-Fernández, N.[1,2*], **Pontes, J. F.**[2], **Torres, M.D.**, **Domínguez, H.**[1], **Grenha, A.**[2]

[1]Department of Chemical Engineering, Science Faculty, University of Vigo, 32004 Ourense, Spain
[2]Centre for Marine Sciences (CCMAR), Universidade do Algarve, 8005-139 Faro, Portugal
**noelia.florez@uvigo.es*

Seaweeds have in their cell wall compounds with interest in several fields due to their biological properties. Polysaccharides as fucoidan in brown, ulvan in green and carrageenan in red algae are the most important polymers in these raw materials. Focusing on fucoidan, this polymer could be defined as a sulphated polysaccharide, described in the literature to exhibit biological properties owing to its structure and composition [1]. In order to obtain fucoidan, extraction technologies that include conventional, as maceration or distillation, and eco-friendly, as subcritical water extraction or ultrasound assisted extraction have been used. Besides, membrane fractionation has the possibility to concentrate the bioactive compounds to improve their properties. The formulation of polymeric nanoparticles can be performed by polyelectrolyte complexation, which requires two materials with opposite charges. In this context, chitosan is a marine polymer comprised of *N*-acetylglucosamine and D-glucosamine units, with low toxicity and biocompatibility, suitable properties to biomedicine or cosmetic fields. The aim of this work was to obtain active membrane fraction from *Laminaria ochroleuca* alga using eco-friendly treatment and evaluate the ability to produce polymeric nanoparticles using a selected membrane fraction.

The extraction was performed according to a previous work [2], being the temperature selected 160 °C. The membrane fractionation was also carried out according to a previous work [3]. The fraction with higher content on antioxidant properties and phenolic content was selected to continue to the formulation of particulate systems. Extract membrane fraction from *L. ochroleuca* was dissolved in ultrapure water, while chitosan was dissolved in 1% (v/v) acetic acid, both being filtered afterwards (0.45 µm and 5-13 µm, respectively). Chitosan/extract nanoparticles were prepared according to a previously reported method [4]. Varied mass ratios of polymer/extract were tested to formulate the nanoparticles, between 4/1 and 1/4. The nanoparticles were characterised regarding physicochemical characteristics (size and zeta potential) using a Zetasizer Nano ZS (Malvern Panalytical, UK). The experiments were done at least in triplicate.

Owing to the antioxidant properties, the retentate of 100 kDa was selected. The nanoparticle formulations showed sizes under 400 nm and zeta potential values could be associated to the charge density of the chitosan. This work allowed to study the characteristics of polymeric nanoparticles, showing attractive results for several applications. The possible future next step could be evaluating the release of phenolic compounds and the biomolecules with antioxidant properties, could be evaluated in correlation with the time.

Acknowledgements

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A new approach for assessing silver and titanium dioxide nanoparticles in tap water samples

Justo-Vega Ana[1]*, Domínguez-González Raquel[1], Bermejo-Barrera P.[1], Moreda-Piñeiro Antonio[1]

[1]Group of Trace Elements, Spectroscopy and Speciation (GETEE), Materials Institute (iMATUS), Analytical Chemistry, Nutrition and Bromatology Department, Faculty of Chemistry, Santiago de Compostela University.
Avda das Ciencias, s/n 15782, Santiago de Compostela, Spain
ana.justo.vega@rai.usc.es

Mainly due to the unique properties of nanoparticles (NPs), but also of their novelty, NPs are now widely used in many sectors and are of great scientific interest. Titanium dioxide nanoparticles (TiO_2NPs) can be found in a variety of products including cosmetics, food industry articles and paints, and are applied in photocatalytic processes [1]. Whereas silver nanoparticles (AgNPs) are extensively used in medicine, healthcare products, the food industry as well as the cosmetic sector, among others [2].

The widespread use of NPs has led to a growing concern about their impact on both the environment and human health. Indeed, even though NPs are not yet fully regulated, they have been included in lists of emerging pollutants [3]. Therefore, NP assessment in environmental matrices and biological fluids is becoming an important topic and the development of reliable quantification and characterization analytical methods is needed. Although their presence in aquatic systems can be assumed, their concentration is expected to be low. As a result, special considerations must be taken into account during sample pretreatment and determination processes.

In this communication, a new strategy combining surfactant assisted dispersive liquid liquid microextraction (SA-DLLME) with *single-particle* inductively coupled plasma mass spectrometry (spICP-MS) for the selective extraction of TiO_2 and AgNPs from tap water samples is proposed. When working with dwell times in the µs range, one particle at a time can be detected. This technique provides useful information about the number concentration and the particle size distribution of a NP suspension. The developed procedure was comprehensively optimized and further validated.

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Dehydropeptide-Based Self-Assembled Hydrogels: *soft* nanostructured materials for the development of theranostic platforms

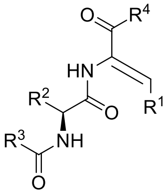
André Carvalho[1,*], **Manuel Bañobre-López**[2] ,**José Alberto Martins**[1], **Paula Margarida Ferreira**[1]

[1]Centre of Chemistry - University of Minho, Campus de Gualtar, 4710-057 Braga,
Portugal;
[2]International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga s/n, 4715- 330
Braga, Portugal; **id9569@alunos.uminho.pt*

Peptide-based self-assembled hydrogels (SAPH) are archetypical highly hydrated porous 3D soft materials produced by entanglement of nanostructured fibres, generated by peptide self-assembly in aqueous media. The hierarchical 3D fibrous nanostructure of SAPH, reminiscent of the extracellular matrix, is conducive to a plethora of applications in biomedicine.[1] The UMinho *Peptide Soft Materials* group contributed to this research field an expedite strategy for the synthesis of dehydropeptides which undergo self-assembly into a variety of nanoarchitectures in aqueous media. Our work established low molecular weight dehydropeptides *N*-capped with bulky aryl groups as exceptional hydrogelators: low critical gelation concentration, tuneable elasticity, proteolytic resistance and NSAID properties. Naproxen and other aryl *N*-capped dehydropeptides were widely explored by our research groups as nanocarriers for drug delivery applications.[2]

Recently, we explored dehydropeptide-based hydrogels as nanoplatforms for the development of theranostics.[3] The properties of dehydropeptide-based hydrogels were augmented with responsiveness to external magnetic fields (Magnetic Hyperthermia; MH) allied to Magnetic Resonance Imaging (MRI) reporting capabilities by incorporation of Superparamagnetic Iron Oxide Nanoparticles (SPION).

In this communication we present an overview of the methodologies developed by the research group for the preparation of aryl *N*-capped peptide-based hydrogels containing non-proteinogenic dehydroamino acids (**Figure 1**).



R^1 - H, Me, Ph; dehydroamino acids
R^2 - proteinigenic amino acids
R^3 - aromatic groups
R^4 = OH, OMe

Figure 2. *N*-capped dehydropeptides developed as efficacious hydrogelators.

The strategies deployed for the preparation and characterization of pristine and magneto-responsive (with incorporated SPION) dehydropeptide hydrogels will be presented and discussed. The effect of hydrogelator structure and concentration and hydrogel network on the MH and MRI reporting properties of the hydrogels will be discussed.

Future avenues for the development of dehydropeptide-based hydrogel theranostic platforms will be discussed.

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Stimulus-responsive liposomes as a smart platform for prednisolone delivery to activated macrophages

Andreia Marinho[1,2,*], Salette Reis[1] and Cláudia Nunes[1]

[1]LAQV, REQUIMTE, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal
[2]LAQV, REQUIMTE, Faculdade de Ciências, Universidade do Porto, R. Campo Alegre s/n, 4169-007 Porto, Portugal
**up2021205710@edu.fc.up.pt*

Inflammation is a biological defense process of the body that occurs in response to harmful stimuli. Despite this, if not properly regulated, it can lead to chronic inflammatory conditions, as is the case with pathologies such as rheumatoid arthritis or osteoarthritis. Fortunately, there are several drug options that help controlling inflammation, including non-steroidal anti-inflammatory drugs, glucocorticoids, and disease-modifying anti-rheumatic drugs. Among these options, prednisolone is considered by the World Health Organization (WHO) to be an essential anti-inflammatory [1]. However, its use is limited due to the various side effects associated with it. To overcome these limitations, in this study pH-sensitive liposomes were developed for targeted administration of prednisolone to activated macrophages [2]. As a targeting strategy for the overexpressed CD44 receptor on activated macrophages [3], functionalization with hyaluronic acid was considered.

Liposomes, produced by the thin-film hydration method, were characterized in terms of hydrodynamic diameter, polydispersity index, zeta potential, and encapsulation efficiency. In addition, the *in vitro* therapeutic performance of pH-sensitive liposomes was evaluated through drug release studies that mimic biological conditions (pH 7.4 and pH 5.0), cytotoxicity studies (L929, RAW 264.7, and THP-1 cell lines), and hemolysis studies. The ability of liposomes to regulate the release of inflammatory mediators was also verified.

Overall, the liposomes were revealed to be a promising smart platform to enhance the therapeutic efficacy and efficiency of prednisolone on chronic inflammation long-term treatment.

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New Approaches for CO_2 Methanation in Ionic Liquid Systems

C.I. Melo[1], A.B. Paninho[1], J. Carvalho[1], C. Pires[1], B.F. Machado[2], J.C.B. Lopes[2], A.V.M. Nunes[1], L. C. Branco[1*]

[1] LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal
[2] CoLAB Net4CO2 - Network for a Sustainable CO2 Economy, Porto, Portugal;
** cim16112@campus.fct.unl.pt*

Commonly known as greenhouse gas, CO_2 has as immense potential as a (C1) building block to produce value-added compounds. From CO_2 hydrogenation it's possible to obtain a wide range of chemicals, such as formic acid, formate, methane, lower olefins, higher hydrocarbons, methanol, higher alcohols, and others, most of which can be used as fuels. However, one of the greatest obstacles with CO_2 conversion is the fact that it is a very stable molecule, thus requiring a large amount of energy for its activation [1].

Using a biphasic system containing excess CO_2 in the gas phase and imidazolium ionic liquid (IL) in the stationary phase, CO_2 methanation can be achieved at relatively mild temperatures. In this process IL's unique properties promote the formation and stabilization of highly active nanoparticles capable of catalysing the reaction. After optimization, an 84% yield was obtained at 150ºC [2,3].

We have recently studied a series of new approaches to make this reaction more efficient and sustainable to convert it into a continuous process. Diffusion limitation and semi-continuous studies were performed, a lower pressure study was made, and the use of porous supports was explored.

Bio-based aerogels are porous structures with relevant properties such as large surface areas, high porosity and low bulk density, making them very attractive for catalytic applications [4].

The application of these aerogels revealed that they are as an efficient support for the catalytic NPs/IL system, capable of increasing NPs stabilization and reducing the amount of catalyst required.

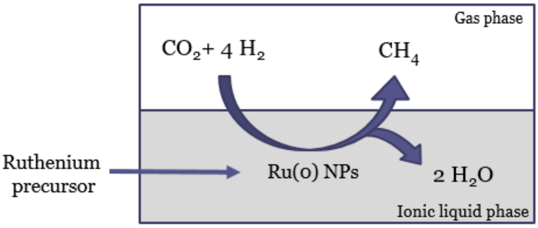

Fig.1. CO_2 methanation scheme under reaction conditions.

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Mitoxantrone-loaded lipid nanoparticles as a promising therapeutic strategy for breast cancer: two different functionalization strategies

Andreia Granja[1,*], Maria Francisca Bento[1], Tânia Moniz[1] Cláudia Nunes[1] , Célia T. Sousa[2,3] and Salette Reis[1]

[1] LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313, Porto, Portugal.
[2] IFIMUP-IN and Dep. Física e Astronomia, Faculdade de Ciências, Universidade do Porto, Rua Campo Alegre 687, 4169 - 007 Porto, Portugal
[3] Departamento de Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid (UAM), Campus de Cantoblanco, C/ Francisco Tomás y Valiente, 7, M 12 604 - 28049, Madrid, Spain
*up201100714@up.pt

Breast cancer is currently the major cause of cancer-related deaths in women worldwide, with 2.3 million new cases and 685 000 associated deaths reported in 2020 [1]. The conventional breast cancer therapeutic modalities often lead to severe systemic side-effects, due to their limited selectivity towards tumor tissues. Nanotechnology can have a significant contribute in improving the efficacy of these therapeutics by increasing their accumulation in tumor tissues and reducing the associated systemic toxicity. This phenomenon can be enhanced by the development of active targeting strategies in which nanoparticles can be functionalized with different targeting ligands that can bind to specific receptors overexpressed in cancer cells. Lipid nanoparticles may offer some advantages over other types of nanoparticles, as they can be produced using very simple, affordable and organic solvent-free methods.

The purpose of this work is to develop lipid nanoparticles for the entrapment of the chemotherapeutic drug Mitoxantrone. Nanoparticles were produced using a simple green method and revealed adequate characteristics for intravenous administration and tumor passive targeting [2]. To improve the accumulation in the tumor region, two different functionalization strategies based on folic acid [2] and hyaluronic acid were then developed. *In vitro* drug release assays demonstrated a higher release at acidic than physiological environment. Moreover, the nanoparticles were found to be non-hemolytic and could maintain or even improve the anti-cancer activity of the drug in the breast cancer cell line MCF-7. Finally, both functionalization strategies led to an enhanced cancer cellular uptake, as assessed by both flow cytometry and confocal microscopy [2].

Overall these data demonstrated that the developed nanoformulation is an efficient mitoxantrone delivery vehicle, highlighting the efficacy of the two active targeting strategies explored. Taking into consideration the benefits of this nanosystem, namely its low-cost production and functionalization, a scale-up and clinical translation may be feasible, after the appropriate *in vivo* and clinical studies.

Acknowledgements

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Advanced LIBS based on nanosilicon and lignocellulosic-based composites

Carlos Marchante[1*], José Manuel Míguez[2], Volker Hoffmann[2], Antonio Pérez[2], Alicia Bañón[3], Cristina Antuña[1], María del Mar Castro[1], Rosalía Noguerol[3*]

[1] ENSO INNOVATION, Parque empresarial de Alvedro, Rúa H, 22, 15180 Culleredo, A Coruña
[2] FERROGLOBE INNOVATION, Paseo Castellana 259d 49 Torre Espacio, 28046, Madrid
[3] CETIM, Parque empresarial de Alvedro, Rúa H, 20, 15180 Culleredo, A Coruña
[*cmarchante@ensoinnovation.com; rnoguerol@cetim.es*]

The transition to a climate-neutral Europe requires fundamental changes. Batteries are a key enabling technology for this change, mainly in the electromobility sector. Recent demand for electric and hybrid vehicles, coupled with a reduction in prices, has caused **lithium-ion batteries** (LIBs) to become increasingly popular battery technology. Although the overall performance of automotive LIBs has improved greatly in recent years, major challenges and opportunities remain. Batteries with higher energy density, increasing lifetime and reliability, improved safety and environmental sustainability, and with cost-effective large-scale production, are key aspect to have into account [1].

Silicon is considered as one of the most promising high-capacity anode materials for application in LIBs. Abundance, low cost or its environmentally friendly nature makes Si an attractive alternative to the conventional graphite anodes. However, the successful implementation of Si-based anodes in LIBs is seriously hindered by their huge volume expansion (more than 300% in the lithiated state) and the instability of the solid-electrolyte interphase layer (SEI) [2]. Therefore, poor cycle-life of silicon materials results from pulverization during these huge volumetric fluctuations. To accommodate the huge volumetric changes several strategies have been developed. Among them, reducing the active particle size to the nanometer range has been considered one effective strategy. Another approach to overcome the volume change during cycling is to form a composite material. **Lignocellulosic feedstock** is considered as an alternative material to be used as biocarbon precursor to be employed into the emerging novel applications for biocarbon based LIBs composite materials. Renewability, biodegradability and excellent properties are of high interest [3].

Therefore, research and development of technologically advanced, highly energy efficient and environmentally sustainable electrochemical solutions based on silicon has been considered. The study of sustainable compounds mainly based on biochars from high impact lignocellulosic species/wastes in Galicia has also been taken into account. Silicon nanomaterials has been obtained and combined with lignocellulosic materials to give place to high-performance anodes. Their electrochemical properties have been tested through electrochemical analysis: CR2032 button-type coin cells were used to analyse the electrochemical measurements of all prepared samples (Fig. 1).

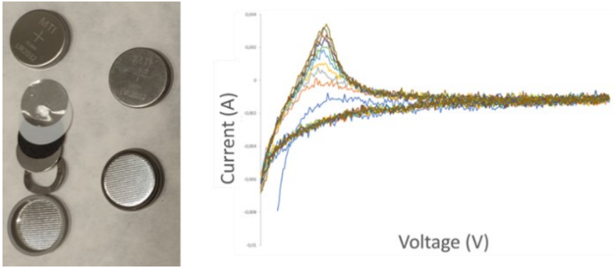

Fig. 1. Button-type coin cells and electrochemical analysis

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Searching for the chemistry that works: formulating hydrogels and nanogels towards atopic dermatitis therapy

Ana Isabel Barbosa[1, 2], Sofia Costa Lima[3, *], Salette Reis[1]

[1]LAQV, REQUIMTE, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal
[2]ICBAS, School of Medicine and Biomedical Sciences, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal
[3]LAQV, REQUIMTE, ICBAS, School of Medicine and Biomedical Sciences, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal
**slima@icbas.up.pt*

Atopic dermatitis (AD) is a chronic and relapsing inflammatory skin disease affecting children and adults worldwide. Among the most common manifestations, it is characterized by intense itch which causes redness, dryness, and bleeding with further damaging of the skin barrier. Several pathophysiological mechanisms contribute to AD clinical manifestations. Current treatments include topical moisturizers and anti-inflammatory agents, such as corticosteroids (e.g. betamethasone), calcineurin inhibitors and systemic immunosuppressants, but the search for new nanotechnological solutions is necessary to cope with the broad manifestations of this condition.

Polysaccharides from marine origin benefit from individual anti-inflammatory activity and hydrogel forming capacities for cutaneous application. Hydrogels have been described as desirable drug delivery systems when compared to other topically applied galenic forms, especially due to higher water content with associated cooling and hydration effects, reduced transepidermal water loss, longer drug absorption, and high skin biocompatibility because of natural origin polymeric structures [1]. The strategy to use hydrogels for AD treatment is very recent, reformulating different corticosteroids into hydrogels, as an alternative to conventional creams and ointments [2]. Among the main positive outcomes, it is seen that hydrogels are well tolerated, bioequivalent, promote better skin permeation, higher delivered doses, and water retention.

This work aimed to explore the potentialities of marine-based hydrogels for targeted delivery of betamethasone *per se* or incorporated in lipid nanoparticles (nanogels), to maximize its local effect on skin layers, avoiding the side effects. After physicochemical characterization, skin permeation, and biocompatibility studies, the systems were found to present high betamethasone drug content, pseudoplastic rheological behaviour, retain betamethasone in skin layers, biocompatible towards fibroblasts and keratinocytes, and presented anti-inflammatory potential.

These platforms can represent an interesting strategy to design new therapeutic approaches for AD.

Acknowledgements

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Biomass derived components to improve energy storage systems

María del Mar Castro[1*], Alicia Bañón[2], Cristina Antuña[1], Carlos Marchante[1], Rosalía Noguerol[2]

[1] ENSO INNOVATTION, Parque empresarial de Alvedro, Rúa H, 22, 15180 Culleredo, A Coruña
[2] CETIM, Parque empresarial de Alvedro, Rúa H, 20, 15180 Culleredo, A Coruña
[*mcastro@ensoinnovation.com]

Biomass materials are of great interest in high-energy rechargeable batteries due to their appealing merits of sustainability, environmental benefits, and more importantly, structural/compositional versatilities, abundant functional groups and many other unique physicochemical properties. These unique physicochemical properties offer an emerging opportunity for compatibility with storage systems, and in particular for advanced lithium-ion batteries. Uncontrollable lithium dendrite growth, large electrode volume variation, poor charge conductivities of active species, dissolution and diffusion of electrochemical intermediates, are some of the main limitations of today's batteries, which considerably result in low Coulombic efficiency, rapid capacity degradation, inferior cycling stability, and severe safety hazards. Transition metals and metal oxides are emerging as promising replacements to graphite anodes. However, the poor conductivity, large volume expansion, and strong aggregation tendency pose a threat to battery performance and stability. The challenges facing lithium-ion batteries could be overcome by using biomass-based materials. One of the strategies to overcome these shortfalls in the electrodes is the use of bio carbon-based materials (BC). BC can be added to produce composite structures with improved conductivity and the added carbon acts as a buffer against volume expansion. The porous and tunable nature of BC is favorable for the permeation of the active materials through the pores to achieve proper adsorption. The conductive nature of BC facilitates the charge transfer and improves overall cycling stability, however, the mechanisms responsible for lithium transport through the BC structure is still not well understood [1]. In addition to being part of electrodes as BC, lignocellulosic materials have interesting properties for use in electrolytes or separators. In terms of electrolyte, natural polymers have intrinsic superiority in forming ionically cross-linked networks owing to intramolecular and intermolecular interaction in water solution, exhibited better safety, stability, and reliability in comparison with organic electrolytes. Regarding separators, compared to the commercialized polyolefin separator, the cellulose-based nanofibrous separator displayed not only higher ionic conductivity, but also improved thermal-resistance property with no shrinkage up to 200 °C, rendering the LIBs higher rate capability and better capacity retention [2].

Battery components based on lignocellulosic materials will be studied and developed to significantly improve the energy density, cost and sustainability of lithium-ion batteries. Novel research in sustainable materials manufacturing and their synergistic combinations for the different components of the electrochemical cell (anode, electrolyte and separators) will be considered. The electrochemical evaluation will be carried out through the preparation of coin and pouch cells (Fig. 1).

Fig. 1. Composite electrode, electrolyte, separator and electrochemical analysis

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Characterization of κ- and ι- carrageenans-based hydrogels as potential vehicles in skin delivery

Zinaida Shakel[1], **Sofia A. Costa Lima[2*]**, **Salette Reis[1]**

[1]LAQV, REQUIMTE, Faculty of Pharmacy, University of Porto, Portugal
[2]LAQV, REQUIMTE, ICBAS, School of Medicine and Biomedical Sciences,
University of Porto, Portugal
**slima@icbas.up.pt*

Hydrogels are three-dimensional polymeric networks with value for pharmaceutical, biomedical and cosmetical applications due to their biocompatibility with the human body [1]. Carrageenan (CRG) is a natural polysaccharide extracted from edible red seaweeds, generally applicable as a gelling agent in food. CRG has antioxidant properties [2] and, on the contrary, induces inflammatory responses in the biological systems in parenteral application [3]. To minimize the adverse effects, we made hybrid hydrogels by combining synthetic (polyvinyl pyrrolidone (PVP)) and natural (CRG) polymers. This work aims to investigate the potential of hydrogels based on PVP and κ- (k-CRG) or ι- carrageenan (i-CRG) for safe skin delivery of transethosomes.

The transethosomes composed of egg yolk phosphatidylcholine, ethanol and surface-active agent (tween 80) were obtained using the thin-film hydration method. The polymer structure was characterised by Fourier transform infrared spectrum (FTIR) and rheological measurements (viscosity, thixotropy, shear rate, temperature stability). The antioxidant activity was analyzed by ABTS assay. Cell viability assays were carried out in keratinocytes (HaCaT), and fibroblasts (L929) cell lines. Quantification of cytokines IL-4, IL-6, IL-8 and TNF-α secreted by THP-1 differentiated macrophages was performed by enzyme-linked immunosorbent assay (ELISA). The pig ear skin was used as a model for permeability assay.

Produced hybrid hydrogels showed storage stability for up to 10 weeks according to rheological properties. i-CRG-based hydrogels demonstrated a thixotropic behaviour opposite to k-CRG and exhibited higher antioxidant activity than k-CRG. For fibroblasts, i-CRG hydrogel is toxic at 125 mg/mL but k-CRG can be used up to 250 mg/mL. Thus, k-CRG-based hydrogel is more favourable as a promising candidate to proceed with the studies.

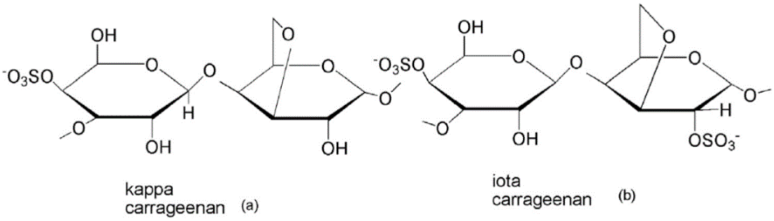

Fig.1. Chemical structure of κ- and ι- carrageenans

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Quantum dots and chemometrics: potential and advantages

João L.M. Santos, Rafael C. Castro, Ricardo N. M. J. Páscoa, M. Lúcia M. F. S. Saraiva, Sarmento J. Mazivila, David S.M. Ribeiro

LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry,
Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313
Porto, Portugal
** email: joaoalms@ff.up.pt*

Quantum-dots (QDs) are fluorescent nanomaterials with exquisite optical and chemical properties that encompass broad absorption bands, narrow symmetric emission spectra, tunable size-dependent band-gap, high quantum yields and high photochemical stability [1].

QDs properties have endorsed the application of quantum dots as sensing platforms in multiple methodologies that explored the analyte-triggered modulation of QDs photoluminescence, either by quenching or enhancing mechanisms, or even FRET processes [2].

However, the higher reactivity of these nanomaterials significantly limited the selectivity of the determinations, particularly in the case of samples with interfering species or complex matrices, demanding the utilization of complementary selectivity enhancing strategies.

The combination of QDs, as fluorescence sensing platforms, and chemometrics, to analyze the PL data they provide, could be a straightforward strategy to circumvent selectivity issues without the need for post-synthesis QDs functionalization, even allowing the possibility of exploit the so-called second-order advantage [3].

Acknowledgments

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Verteporfin-loaded lipid nanoparticles as an effective approach for cancer photodynamic therapy

Andreia Granja[1,*], Tomás Mendes[1], and Salette Reis[1]

[1] LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313, Porto, Portugal.
* up201100714@up.pt

Cancer is the main cause of morbidity and mortality worldwide. In 2020, 19.3 million new cases were diagnosed and almost 10 million cancer-related deaths were reported [1]. The limitations of the current cancer therapeutic highlight the need to develop new treatment modalities. Photodynamic therapy (PDT) is a minimally invasive procedure which results from the interaction of three main components: a photosensitizer, a light source and molecular oxygen [2]. Upon light irradiation of appropriate wavelength, the photosensitizer, once internalized into the cancer cell, will trigger different photophysical and photochemical reactions, which culminate in the production of reactive oxygen species, leading to cancer cell death [2]. Verteporfin is a protoporphyrin derivative clinically approved as a photosensitizer for age-related macular degeneration and currently under clinical trials for the treatment of different cancer types [3]. Nevertheless, its poor solubility in aqueous solution and low tumor selectivity can limit the clinical use of this molecule. Taking this into account, the purpose of this work was to develop lipid nanoparticles for the entrapment of the photosensitizer Verteporfin to improve its water solubility and selectivity towards cancer cells. Nanoparticles were produced using a simple and affordable method and an encapsulation efficiency of more than 95% was obtained, along with particle sizes suitable for intravenous administration. Moreover, the nanoformulations were non-hemolytic and revealed a low dark toxicity, in normal (L929) and cancer (MCF-7) cells. Upon light irradiation using a LED light source (690 nm) at low light doses, a high cancer cell death was obtained at the same range of concentrations tested in dark conditions, demonstrating that the encapsulation of the drug could maintain its high PDT effect. Additionally, an increased production of reactive oxygen species and induction of apoptosis in MCF-7 cells occurred following light irradiation, demonstrating once again the efficacy of the PDT using verteporfin-loaded lipid nanoparticles.

Overall this data suggests that the lipid nanoformulation developed is an effective verteporfin delivery vehicle, holding great promise for a future PDT clinical application.

Acknowledgements

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QUÍMICA DE POLÍMEROS

Silylated poly(azomethine)s with possible applications in the optoelectronic field. Synthesis and characterization

Claudio A. Terraza[1,*], Alain Tundidor-Camba[1], Patricio A. Sobarzo[1], René A. Hauyon[1], Luis E. García[1], Jean Medina[1], Alexis González[1], Constanza Camilla-Piña[1], Ignacio Jessop[2], Carmen González-Henríquez[3]

[1]Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile
[2]Universidad de Tarapacá, Av. General Velásquez 1775, Arica, Chile
[3]Universidad Tecnológica Metropolitana, Las Palmeras 3360, Macul, Santiago, Chile
**cterraza@uc.cl*

π-Conjugated poly(azomethine)s (PAZs) has been widely studied in recent decades due to their optoelectronic, thermal and morphological properties in advanced optoelectronic applications as active- or buffer-layers in polymer solar cells (PSCs) and polymer light-emitting diodes (PLEDs). [1]

Structural units based on Group IV atoms have been used as moieties that improve processability both thermally and in solubility for advanced materials in optoelectronic devices. [2] Our research group has extensively reported different series of p-conjugated PAZs containing silicon with high aromatic content and interesting optoelectronic, thermal and morphological properties, which allows us to propose them as active materials in the construction of optoelectronic devices (Fig.1). [3] Thus, this work focuses on the design of a series of dimethylsilane/tetraphenylsilane-based PAZs as well as on the study of their optical, electronic, thermal and morphological properties for organic electronics.

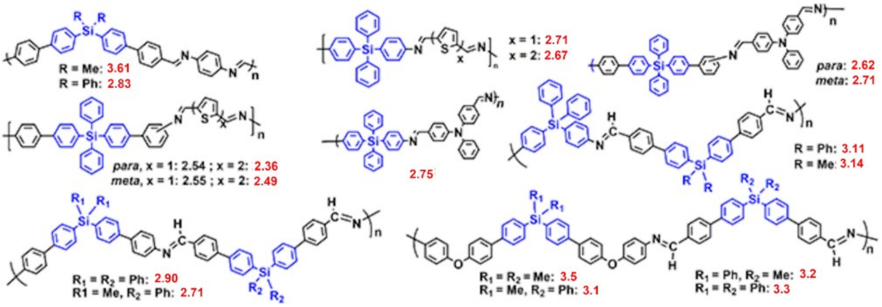

Fig.1. Some TPS/DMS-based PAzMs prepared and their band gaps values (eV).

Acknowledgments

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Cómo minimizar el rechazo de implantes empleando la química click

J.Sánchez-Bodón[1]*, I. Moreno[2], L. Ruiz-Rubio[1,3], L. Pérez-Álvarez[1,3], A.C. Lopes[1,4], J.L Vilas-Vilela[1,3]

[1]Grupo Química Macromolecular, Dpto. Química Física, UPV/EHU, Leioa, España
[2]Grupo Química Macromolecular, Dpto. Química Orgánica e Inorgánica, UPV/EHU, Leioa, España
[3]BCMaterials, Centro Vasco de Materiales, Aplicaciones y Nanoestructuras, Leioa, España
[4]IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, España
**julia.sanchez@ehu.eus*

En la última década, el poli ácido-L láctico (PLLA) ha generado un gran interés en el ámbito biomédico debido a sus prometedoras aplicaciones como sistema liberador de fármacos, apósito o, incluso, prótesis [1-2]. Este poliéster alifático, además de haber demostrado ser biocompatible y biodegradable, posee unas magníficas propiedades físico-químicas como una buena procesabilidad y resistencia mecánica que le convierten en un candidato excepcional para ser empleado en las mencionadas aplicaciones como *coating* para implantes. Sin embargo, la alta hidrofobicidad inherente a este material, además de la ausencia de grupos funcionales en su superficie capaces de atraer células, pueden comprometer la adhesión y proliferación celular para una buena integración. Como consecuencia, se puede desencadenar una respuesta inflamatoria negativa, llegando, incluso, al rechazo del implante. [3]. Por ello, en los últimos años, el diseño y la preparación de materiales con actividad antibacteriana, antiinflamatoria y anticoagulante ha aumentado considerablemente con el objetivo de mejorar la hemocompatibilidad.

En este trabajo, se presenta una estrategia química capaz de anclar de forma permanente un fármaco antiinflamatorio (Indometacina) a la superficie del PLLA. Esta unión covalente, se ha llevado a cabo empleado la reacción *click* entre azidas y alquinos catalizada con cobre. Por tanto, previa a la conjugación del fármaco a la superficie, han sido necesarias las correspondientes derivatizaciones para disponer de los grupos funcionales requeridos. La eficacia de la metodología ha sido estudiada empleando diferentes técnicas y ensayos como resonancia magnética nuclear (RMN), ángulo de contacto, espectroscopia de fotoelectrones de rayos X (XPS) y microscopia de fluorescencia. Además, la capacidad antiinflamatoria de la superficie ha sido estudiada mediante los pertinentes ensayos biológicos [4].

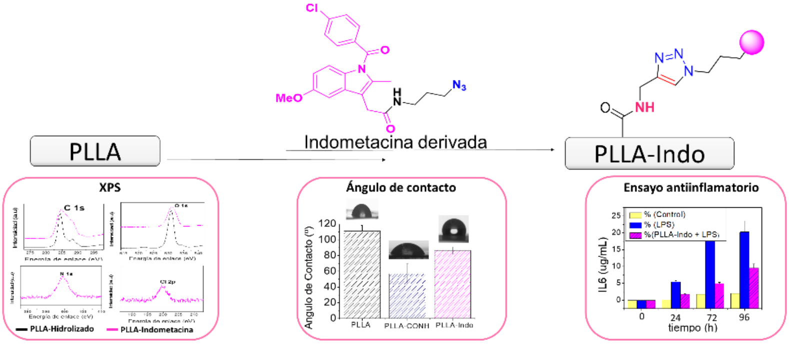

Fig.1. Esquema acortado de la bioconjugación de la indotemacina y sus resultados.

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QUÍMICA ANALÍTICA

Desenvolvemento dun marco analítico para a determinación de contaminantes orgánicos persistentes e móbiles en mostras de urina

María Lage-Díaz[*], **Rosa Montes, Rosario Rodil, José Benito Quintana**

Departamento de Química Analítica, Nutrición e Bromatoloxía, Instituto de Investigación en Análises Químicas e Biolóxicas (IAQBUS), Rúa Constantino Candeira S-N., 15782 Santiago de Compostela, España
* maria.lage.diaz@rai.usc.es

Os compostos orgánicos persistentes e móbiles (PMOCs) debido ás características físico-químicas dos mesmos, móvense con facilidade a través do ciclo da auga acadando a auga de consumo [1]. Se adicionalmente presentan toxicidade poden supor un perigo potencial para a saúde humana. Por iso, nos últimos anos estase a tratar de poñer freo a estas substancias co desenvolvemento de regulamentos adecuados para o seu control [1]. Porén, a metodoloxía analítica para a súa determinación, particularmente en fluídos biolóxicos humanos é practicamente inexistente.

O obxectivo do traballo é sentar as bases analíticas para que nun futuro próximo se poida establecer o nivel de exposición humana a estas substancias a través da análise dos ouriños. Para iso, realizouse unha comparación de diferentes metodoloxías cromatográficas acopladas a espectrometría de masas (MS) que permitan unha mellora na determinación, en urina, dun total de 38 compostos modelo de elevada polaridade e carga variable. Así, estudáronse modos coma a cromatografía líquida de fase reversa (RPLC), de modo mixto (MMLC) e de interacción hidrofílica (HILIC), e a cromatografía de fluídos supercríticos (SFC).

Coa fin de comparar estes modos cromatográficos, estudouse a retención e a forma dos picos obtidos dunha mestura dos compostos modelo en auga ultrapura para RPLC e MMLC e en acetonitrilo para HILIC e SFC, cun total de 9 columnas diferentes. Así, descartáronse 5 columnas e continuouse o estudo coas 4 columnas que proporcionaban os mellores resultados, sendo estas: as columnas Torus Diol e Zorbax Sil de SFC, a columna Trinity P1 de MMLC e a columna Luna C18 de RPLC. Posteriormente, analizáronse os rendementos destas mediante a análise de mostras con adición dos compostos modelo en matriz real (urina). Leváronse a cabo dúas preparación diferentes: *dilute-and-shoot* e extracción en fase sólida (SPE) con cartuchos de Oasis HLB de 60 mg. Estas probas mostraron que os picos dos compostos non se vían afectados en termos de retención ou forma de pico en ningunha das 4 columnas. Si se apreciou diferenza nos efectos de matriz na determinación, onde o método con menor efecto matriz foi o da SFC empregando a columna Torus diol. A validación do método instrumental para 31 PMOCs modelo produciu linealidade e repetibilidade aceptables, e con límites de cuantificación variables entre 0,1 e 250 µg/L.

Por tanto, levouse a cabo un estudo preliminar de preparación de mostra para mellorar a sensibilidade. Realizáronse SPEs con cartuchos Oasis HLB de 60 mg a pH 2,7 e 12. A eficacia de extracción obtida foi adecuada para unha fracción significativa dos compostos. Por outra banda, para os compostos máis polares e iónicos, observouse que se se colocaban cartuchos en serie, estes compostos quedaban retidos no 2º cartucho polo que se procedeu a aumentar a cantidade de adsorbente dos cartuchos a 500 mg. Este cambio favoreceu a adecuada retención dunha fracción maior de compostos, pero non da totalidade. Así pois, estableceuse que a extracción en fase sólida con cartuchos de Oasis HLB é unha metodoloxía de preparación de mostra adecuada para unha fracción dos PMOCs modelo estudados. Por tanto, o traballo futuro dirixirase cara a mellora da etapa de preparación da mostra.

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Optical sensors for amine vapours detection and discrimination

Cláudio M. R. Almeida[1,2,*], **Júlia M. C. S. Magalhães**[2], **Fátima S. Barroso**[3], **Luisa Durães**[1]

[1]University of Coimbra, CIEPQPF, Department of Chemical Engineering, 3030-790, Coimbra, Portugal
[2]REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal
[3]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal.
**claudio@eq.uc.pt*

Amines are a class of molecules with major relevance in biology, pharmaceuticals, and industry. They have unique properties, including basicity, polarity and hydrogen bonding capacity [1]. In humans, amines are present in amino acids, neurotransmitters and nucleic acids extremely important for the life's existence. Also in pharmaceutics, many drugs contain amine functionalities and in industry, amines are present in fertilizers and disinfectants. The so-called biogenic amines can represent a problem in the food industry, since some of them represent a threat to human health.

Due to the high standards of quality control patterns in different industrial sectors, strong demand for cost-effective and reliable analytical devices able to detect and quantify amines has been verified [2]. The application of sensors offers the possibility to achieve on-site information, employing basic sample preparation protocols and simple instrumentation, when compared to standard methodologies such as chromatography.

Optical sensors, essentially those sensors that use the UV-Vis region, present several advantages for on-site inspection operations, mainly because they offer information without the need for complex analytical instruments. However, most optical sensors for amines detection have poor selectivity and resolution [3]. Thus, in this work, we report dyes- and lanthanides-based optical sensors for the determination of amines in vapour.

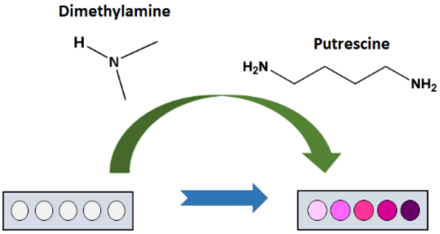

Fig.1. Illustration of optical sensing of amines.

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Screening of organic micropollutants in mollusc and fish samples from the Portuguese coast by combining liquid and gas chromatography with high resolution mass spectrometry

Sandra Méndez[1,*], Daylin López-Castillo[1], Javier López-Vázquez[1], Rosa Montes[1], Joana Raimundo[2], Miguel Caetano[2], Clara Lopes[2], Cátia Figueiredo[2], , Teresa Neuparth[3], Marlene Pinheiro[3,4], Nélson Alves[3,4], Ricardo Capela[3], Susana Barros[3], Hugo Morais[3], Miguel. M. Santos[3,4],José Benito Quintana[1], Rosario Rodil[1]

[1] Institute of Research on Chemical and Biological Analysis (IAQBUS), University of Santiago de Compostela, Santiago de Compostela, Spain.
[2] IPMA – Portuguese Institute for Sea and Atmosphere, Alges, Portugal.
[3] CIMAR/CIIMAR—Interdisciplinary Centre of Marine and Environmental Research, Endocrine Disruptors and Emerging Contaminants Group, Matosinhos, Portugal.
[4] FCUP - Department of Biology, Faculty of Sciences, Universidade do Porto, Porto, Portugal.
**sandramendez.martinez@usc.es*

The presence of organic micropollutants (OMPs), such as persistent organic pollutants (POPs) and contaminants of emerging concern (CECs) has been documented in several aquatic environments. The bioaccumulation of these compounds has become a matter of concern for its possible transfer to the food chain and impact on several wildlife species of the marine environment and human consumers of seafood. Thus, the aim of this work was to apply a wide screening strategy in order to detect different types of OMPs in fish and clam samples from the Portuguese coast.

Liver and muscle *of Trachurus trachurus, Solea solea, Microchirus azevia, Microchirus variegatus, Trisopterus luscus* and the whole body of *Spisula solida* were collected from different areas of the Portuguese coast within the project *CEIC* (Contaminants in commercial species from the Portuguese coast). Sample treatment was performed by three matrix solid-phase dispersion (MSPD) methods [1,2] and then the extracts were analyzed by both liquid and gas chromatography coupled to high-resolution mass spectrometry (LC-HRMS and GC-HRMS).

In this way, a total of 120 OMPs were identified by using two high-resolution [3] and one low-resolution (NIST) spectral libraries. From the substances detected, 58% of them were industrial reagents, 22% were pharmaceuticals and drugs, 12% cosmetic products and 8% pesticides. Besides, the number of OMPs identified using the three different MSPD methods was compared. The method that allowed to detect the highest number of OMPs was the one incorporating silica impregnated with sulfuric acid, likely because of its capacity to remove lipids and other interfering substances.

Among the investigated samples, clams and fish muscle showed a similar contamination profile regardless of the collection area and a higher number of OMPs detected as compared to fish liver, which exhibited a different profile. This may be attributable to the lower amount of liver matrix available and its higher complexity.

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Desenvolvemento dun método para a determinación de biomarcadores do uso de cannabinoides mediante a análise de augas residuais con fins epidemiolóxicas

Carlos Pernas-Fraguela[1,*], Xiana González-Gómez[1], Andrea Estévez-Danta[1], Rosa Montes[1], Rosario Rodil[1], José Benito Quintana[1]

[1]Departamento de Química Analítica, Nutrición e Bromatoloxía, Instituto de Investigación en Análises Químicas e Biolóxicas (IAQBUS), Rúa Constantino Candeira S-N., 15782 Santiago de Compostela, España
**carlos.pernas@rai.usc.es*

O cannabis é a substancia ilegal máis consumida en España e, practicamente, en todo o mundo. Nos últimos anos diversos países e territorios legalizaron o consumo desta droga con fins terapéuticas e/ou recreativas. Ademais, comezaron a comercializarse diversos produtos con cannabidiol (CBD) polos seus supostos beneficios para a saúde, dado que este composto non presenta actividade psicoactiva. Por outra banda, o 9-tetrahidrocannabinol (Δ9-THC) é o composto presente no cannabis con propiedades psicoactivas, o cal está relacionado con numerosos efectos prexudiciais para a saúde [1].

Por todo isto, cómpre dispoñer de metodoloxías que permitan seguir de forma veraz é rápida o consumo de cannabinoides. Neste sentido a análise de augas residuais con fins epidemiolóxicas [2] é unha ferramenta altamente útil e complementaria a outros indicadores, como poden ser as enquisas. Por tanto, o obxectivo deste traballo foi o desenvolvemento dunha metodoloxía analítica para a determinación dos metabolitos hidroxilados e carboxilados do CBD e Δ9-THC, ademais das propias substancias e os seus ácidos precursores, o ácido tetrahidrocannabinólico (THCA) e o ácido cannabidiólico (CBDA). Tamén se determinou a presenza de cannabinol (CBN), de maneira que se poda ter unha visión o máis completa posible do consumo deste tipo de sustancias.

Con esta fin, estudáronse etapas críticas do proceso analítico como son a filtración e o axuste do pH das mostras, así como as diferentes condicións da extracción en fase sólida (*online* e *offline*), e a posterior determinación mediante cromatografía líquida acoplada a espectrometría de masas en tándem (LC–MS/MS). Desta forma, observouse que era necesario lavar os filtros con metanol e engadir patróns marcados isotopicamente antes desta etapa para minimizar e corrixir, respectivamente, a perda por adsorción dos analitos máis hidrófobos na etapa de filtración.

Tras desenvolver a metodoloxía analítica, esta validouse obténdose límites de cuantificación do método inferiores a 5 ng/L e recuperacións analíticas no rango 102–130 %, cunha desviación estándar relativa inferior ao 25 %.

Finalmente, analizáronse mostras de tres localidades españolas distintas. Os resultados amosan presenza de Δ9-THC (10–47 ng/L), dos seus metabolitos (23–201 ng/L) e do seu precursor ácido (34–141 ng/L). No caso do CBD, só foi posible detectar este composto (9–55 ng/L), non sendo posible detectar nin o seu precursor ácido nin os seus metabolitos, o que pode indicar unha exposición tópica pero non un consumo oral nin por inhalación. Pola súa parte, o CBN foi atopado tamén nas tres localizacións (3–14 ng/L).

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Automatic on-line renewable micro-solid-phase extraction hyphenated to tandem mass spectrometry for the determination of uremic toxins in plasma

Sara R. Fernandes[1*], Luisa Barreiros[1], Benedita Sampaio-Maia[2,3], Manuel Miró[4], Marcela A. Segundo[1]

[1] LAQV, REQUIMTE, Dep. Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal
[2] INEB – Instituto Nacional de Engenharia Biomédica/I3S – Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Porto, Portugal
[3] Faculdade de Medicina Dentária, Universidade do Porto, Porto, Portugal
[4] FI-TRACE group, Dep. Chemistry, University of the Balearic Islands, Palma de Mallorca, Spain
saraferns@sapo.pt

Loss of kidney function results in ineffective elimination and, consequently, accumulation of potential toxic substances in the organism [1]. These compounds are named uremic toxins when their accumulation interferes with biological activities. Indoxyl sulfate (INDS) and *p*-cresol sulfate (pCS) are two examples of uremic toxins, whose high concentrations are associated with the development and progression of several pathologies, namely renal (e.g., chronic kidney disease-CKD) and cardiovascular diseases [1]. Thus, the implementation of methodologies that allow accurate measurements of the circulating levels of these compounds in the body is demanded to obtain a fast diagnosis and define the best treatment strategy. Considering this need, an automatic and on-line micro-solid-phase extraction (μSPE) method hyphenated to tandem mass spectrometry (MS/MS) detection for the determination of INDS and pCS in plasma samples was developed.

The μSPE procedure was based on the bead injection (BI) concept implemented in a mesofluidic lab-on-valve (LOV) flow system, using OASIS WAX as anion-exchange sorbent and a mixture of 99% acetonitrile–H_2O (15:85, v/v)–1% (v/v) NH_4OH as eluent. The BI-LOV system was on-line hyphenated to a MS detector, without use of chromatographic column, through a flow network for in-line dilution and by connection to a rotary 6-port high pressure injection valve. The MS was operated in negative electrospray ionization mode (ESI-) and data were acquired in the selected reaction monitoring (SRM) mode (INDS*, m/z* 212.80 > 80.00 and PCS, *m/z* 187.70 > 107.00). All μSPE-BI-LOV-MS steps were implemented by computer programming, rendering enhanced precision on time and flow events. Good linearity ($r^2 > 0.999$) was achieved for concentrations ranging from 18 to 360 mg L^{-1} in plasma. LOQ values of 0.2 mg L^{-1} for INDS and 0.7 mg L^{-1} for pCS in plasma were obtained, corresponding to values detected by MS, after sample treatment and dilution, of 0.1 and 0.4 μg L^{-1}. Furthermore, the greenness of this methodology was evaluated using the AGREE metric [2], and a score of 0.71 was achieved. The developed methodology was successfully applied to the quantification of INDS and pCS in plasma samples obtained from control subjects and CKD patients. Accordingly, this new analytical method can be described as an environmentally friendly methodology that have potential to be applied to the determination of the target compounds in other biomatrices.

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Determination of acid lactase activity resorting to a high-throughput kinetic method

Bruno. J. R. Gregório[1,*], Diego Pettigrosso[1], Luís M. Magalhães[2], Rudolf J. Schneider[3], Marcela A. Segundo[1]

[1] LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal

[2] Present affiliation: Research & Development, BIAL-Portela & Cª, S.A., Coronado (S. Mamede e S. Romão), Portugal

[3] Department of Analytical Chemistry; Reference Materials, Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany

**bruno.jr.gregorio@gmail.com*

Lactose malabsorption is caused by the insufficient or absent synthesis or reduced activity of lactase in the brush border membrane of mucosa of the small intestine. Lactose intolerance, the clinical manifestation of lactose malabsorption, includes clinical signs and symptoms like abdominal pain, flatulence, and diarrhoea, and has an estimated global prevalence >65% [1]. The prevention of the occurrence of these symptoms can be done by replacement of lactose-containing for low-lactose or lactose-free products or by including lactase from exogenous sources in the diet, which have been shown to decrease symptomatology of individuals after ingestion of lactose-containing products [2].

The reference method for the analysis of lactase activity in the diet is described in the Food Chemicals Codex (FCC) [3], however it presents some drawbacks, like the large quantity of solutions used (25 mL of waste generated per sample) and the long assay time (15 min). Hence, this work proposes the development of a high-throughput kinetic miniaturized method in a microplate format that uses β-galactosidase from *A. oryzae* and the fluorescent probe fluorescein di(β-D-galactopyranoside), where the first 2 minutes of reaction are monitored, the initial rate of reaction is determined, and converted to FCC units by calibrating with an FCC tested enzyme. This reduction in assay time coupled to the generation of just 200 µL of waste per sample and the possibility of testing an estimate of 180 samples per hour circumvents the drawbacks of the aforementioned method. Analytical validation of the method was performed by evaluating the acid lactase activity of the enzyme present in different commercially available food supplements, providing results comparable to the reference method.

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Concanavalin A biosensor for evaluation of biopharmaceuticals

Diana R. Cunha[*], **Marcela A. Segundo, M. Beatriz Quinaz**

LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-213 Porto, Portugal.

**dianarlcunha@gmail.com*

Several biopharmaceuticals are glycosylated, also named glycoproteins, derived from a biological source [1, 2]. Glycosylation of proteins is a complex post-translation modification. Glycans or carbohydrates are inserted at specific sites in the recombinant protein backbone or antibodies. This modification can directly affect their biological activity, molecular stability, safety, pharmacokinetics/pharmacodynamics, immunogenicity, and efficacy. Therefore, glycan moieties must be adequately analyzed and controlled throughout to ensure quality. However, the intrinsic complexity of protein glycosylation results in a high analytical effort [3-5].

During the development of therapeutic glycoproteins or biosimilars, assessing specific glycosylation attributes, such as glycosylation site, the glycan structure and their abundance is crucial. The analytical methods usually applied for this analysis are capillary electrophoresis, isoelectric focusing, high-performance liquid chromatography, and mass spectrometry. However, these methods are tedious, and these methods are associated with elevated costs, high-maintenance equipment, highly specialized operators, and intensive process [6-9]. Therefore, biosensors have attracted considerable interest due to advantages including cost-effectiveness, short analysis time, easy-to-use, and miniaturization [10].

In this context, lectins are glycan-binding proteins with specific binding affinity to free carbohydrates or glycoproteins. Lectins have been used in the construction of biosensors for the detection of specific glycoproteins on human serum and glycoprofiling [11, 12]. Therefore, an impedimetric biosensor was developed for the detection and evaluation of biopharmaceuticals, using Concanavalin A (Con A) as the biorecognition element. The increase in the biosensor's electron transfer resistance, after sample incubation, monitored by electrochemical impedance spectroscopy, confirmed the lectin recognition and complex formation between Con A and glycoproteins containing mannose or glucose. The lectin was immobilized on a mixed self-assembled monolayer formed by 3,3′-dithiodipropionic acid di(N-hydroxysuccinimide ester) for covalent immobilization of Con A. For biosensor optimization, invertase from baker´s yeasts was used as a model glycoprotein due to its high content in mannose. Current work is focused on the evaluation of the biosensor concerning its applicability for the identification and characterization of biopharmaceuticals.

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Estudo do emprego de drogas ilícitas, alcohol e tabaco en España e Portugal durante a crise da COVID-19 en 2020 a través da análise de augas residuais con fins epidemiolóxicas

Andrea Estévez-Danta[1, *], Lubertus Bijlsma[2], Ricardo Capela[3], Rafael Cela [1], Alberto Celma[2], Félix Hernández[2], Unax Lertxundi[4], João Matias[5], Rosa Montes [1], Gorka Orive[4], Ailette Prieto[6], Miguel M. Santos[3], Rosario Rodil [1], José Benito Quintana[1]

[1]Instituto de Investigación en Análises Químicas e Biolóxicas (IAQBUS), R. Constantino Candeira S.N., Santiago de Compostela, España
[2]Instituto de Investigación de Pesticidas e Auga, Av. Sos Baynat S-N., Castellón, España
[3] Centro Interdisciplinario de Investigación Mariña e Medioambiental (CIMAR) e Universidade do Porto, Av. General Norton de Matos S-N., Matosinhos, Portugal
[4] Instituto de Investigación Sanitaria Bioaraba, R. Alava 43, Vitoria-Gasteiz, España
[5] Observatorio Europeo das Drogas e as Toxicomanías, 1249-289, Lisboa, Portugal
[6] Centro de Investigación de Bioloxía Mariña Experimental e Biotecnoloxía de Plentzia, Universidade do País Vasco, R. Areatza Pasealekua S-N., Plentzia, España

O virus da COVID-19 estendeuse rapidamente por todo o mundo no ano 2020, o cal obrigou a impor peches perimétricos, afectando a mobilidade e as actividades esenciais. Coa fin de poder establecer o impacto real do confinamento no consumo de drogas, tanto lícitas (alcohol e tabaco) como ilícitas, cómpre dispoñer de ferramentas que nos permitan obter información veraz e a tempo real da situación actual. Dende os inicios do século XXI, a análise de augas residuais con fins epidemiolóxicas (WBE, do seu nome en inglés) converteuse nunha metodoloxía moi útil para observar os patróns de abuso a nivel local. Por todo isto, neste estudo pretendeuse investigar o emprego de drogas ilícitas (anfetamina, metanfetamina, éxtase, cocaína e cannabis), alcohol e tabaco durante os primeiros meses (Marzo-Xullo do 2020) das restricións causadas pola crise da COVID-19 en catro cidades españolas (Bilbao e a súa área metropolitana, Vitoria-Gasteiz, Castellón e Santiago de Compostela) e dúas portuguesas (Porto e Vila do Conde), empregando a WBE. A análise de drogas ilícitas, levouse a cabo mediante unha primeira etapa de extracción en fase sólida (SPE), e a posterior cuantificación das mostras con cromatografía líquida acoplada a espectrometría de masas en tándem (LC-MS/MS) [1]. Para algunhas das mostras realizouse tamén unha análise enantiomérica [2]. A análise de alcohol e tabaco foi efectuada mediante inxección directa no equipo de LC-MS/MS, previa desconxugación encimática para os metabolitos da nicotina [3,4].

Os resultados mostraron que a metanfetamina non foi detectada en ningunha das cidades analizadas, mentres que a anfetamina só foi detectada en dúas cidades, pertencentes a comunidade autónoma do País Vasco (Bilbao e Vitoria-Gasteiz). O resto das substancias de estudo foron detectadas en todas as áreas investigadas [5]. Polo xeral, non se observaron cambios significativos no consumo destas substancias respecto de anos anteriores, excepto para a cocaína. Por último, cabe destacar que se confirmaron, mediante análise enantiomérico, dous eventos de descarga directa de éxtase no sistema de sumidoiros de Santiago de Compostela e Bilbao.

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Assessing the presence of organic micropollutants in surface water

V. Fernández-Fernández*, A.M. Rodríguez de Blas, M. Ramil, R. Cela, I. Rodríguez

[1] Department of Analytical Chemistry, Nutrition and Food Sciences. Research Institute on Chemical and Biological Analysis (IAQBUS). Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain.

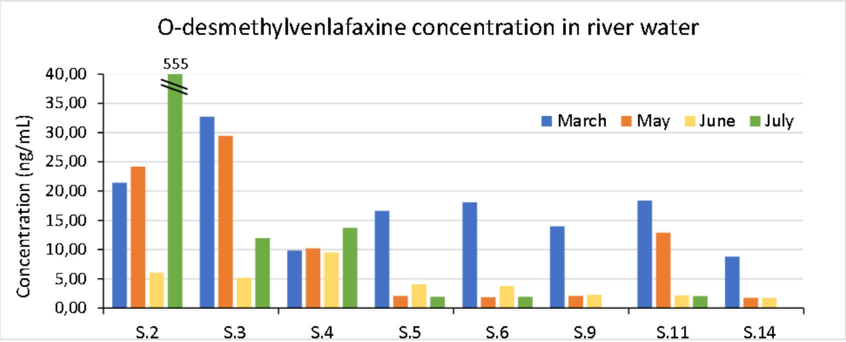
**victoriafernandez.fernandez@ucs.es*

The number of synthetic chemicals identified in municipal sewage water treatment plants (STPs) increased steady for the last two decades. Some of them are poorly removed during conventional water treatments, being discharged to the receiving media, in most case surface waters. Thus, STPs are recognized as local sources of organic micro-contaminants (particularly ingredients from personal care products and pharmaceuticals) in the water media. Intensive agriculture areas might also contribute to pollution of water masses due to the misuse of pesticides, atmospheric drift and leaching of these compounds from treated fields to the water phase. In some cases, the levels of micro-contaminants might exceed their environmental effect, and/or environmental quality thresholds, becoming a threat for the aquatic biodiversity, and even the production of tap water for populations in the same watershed.

Herein, we provide results obtained for a selection of 79 compounds, corresponding to agriculture use pesticides and pharmaceuticals, in water samples obtained at four different dates, from 3 rivers with different pressure of residential and agriculture activities, some small streams draining agriculture fields, and springs of groundwater. Compounds were determined using an automated procedure combining solid-phase extraction (SPE) on-line coupled to LC-ESI-MS/MS.

Around 50% of selected compounds were detected in some of the processed samples. In certain sampling places, systematic presence of pesticides residues was noticed. Some of them, such as the insecticide methoxyfenozide, was even detected in the springs of groundwater. However, as a general rule, the higher number of compounds above method LOQs corresponded to pharmaceuticals, not only in small rivers directly affected by sewage water discharges, but also in a large dam, 20 km downstream the closest STP. Some of the detected pharmaceuticals, such as certain cardiovascular drugs (i.e. olmesartan), the psychiatric drug venlafaxine and the drug metabolites O-desmethylvenlafaxine and valsartan acid, were measured above their predicted non-effect environmental concentrations (PNEC) for the most sensitive fresh water organism. These compounds were identified as potential hazards to the aquatic environment; moreover, they are potential indicators of fresh water contamination, with detection frequencies above 70% in the set of processed samples and values close to 100% in case of river water.

Fig. 2. Concentration of O-desmethylvenlafaxine in different sampling campaigns



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Immobilization of CYP3A4 on surface-modified electrodes: assessment of electroanalytical and electrocatalytic properties

Carina S.P.Vieira[*], **Marcela A. Segundo, Alberto N. Araújo**

LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal.

**up201304074@up.pt*

Cytochrome P450 is a family of heme proteins that catalyze the NADPH-dependent monooxygenation of several compounds [1]. Five CYP enzymes are involved in the metabolism of 95% of drugs, foreign chemicals, and endogenic compounds in the human body [1]. The study of CYP reactions is important in drug development, for the screening of potential substrates or inhibitors and their interactions [1]. In biological systems are necessary electron donors such as NADPH or NADH and electron transfer mediators [1]. Alternatively, electrochemical methods simplify the evaluation of CYP catalysis since the electrode can work as an electron source, replacing partner proteins such as NADPH reductase [1].

The study of the catalytic activity of P450 enzymes adsorbed on the surface of unmodified electrodes is very difficult, due to low catalytic activity and heterogeneous electron transfer [2]. The enzyme orientation and immobilization on the electrode surface, as well as the substrate access, are critical steps in the development of an enzymatic biosensor, determining the sensor response [2]. Cross-linked hydrogels are usually used for the immobilization of enzymes since they stabilize proteins through electrostatic forces and create a microenvironment for optimal enzyme activity on the electrode surface [3]. Graphite pencil leads can be used as working electrodes because they show good sensitivity, reproducibility, high electrical conductivity, minimal background current, and are a green tool for electrochemical analysis. The lead is a mixture of graphite, wax and clay in different proportions. The common HB lead consists in a mixture of around 68% of graphite, 26% of clay and 5% of wax [4]. Nano structuring of their active surfaces can be done with different materials, like carbon nanotubes (CNTs), graphene, carbon dots. Particularly CNTs present optimal chemical and physical properties, like biocompatibility, high electron transfer kinetics, and high sensitivity [5].

The present study aimed to compare different strategies for the immobilization of cytochrome CYP3A4 on the tip surface of HB pencil leads 0.9 mm, with or without previous surface modification, aiming its robustness as biosensor and ability to get acceptable results by cyclic voltammetry. The assessment was conduct either in the absence or presence of the oxygen cofactor, i.e. under anaerobic (N_2 purging) or aerobic conditions, using erythromycin as substrate. The best immobilization strategy was based on a mixture of 70 µL of a 5 mg/mL solution of pyrene-linear poly(ethylenimine), 0.1 mg of multiwalled carbon nanotubes, 30 µL of 10 mg/mL CYP3A4 enzyme solution and 3.75 µL of 13% vol. ethyleneglycol diglycidyl ether, and then poured 3 µL on the pencil lead surface, which rendered a typical Michaelis-Menten kinetics. Hence, this study provided an initial step to improve the immobilization of CYP3A4 on graphite electrodes and to proceed with the metabolism assessment.

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Valorização de espécies mediterrânicas subutilizadas: obtenção de óleo essencial com propriedades bioativas

Virginie Xavier[1,2], Tiane C. Finimundy[1,2], Joana S. Amaral[1,2], Ricardo C. Calhelha[1,2], Josiana Vaz[1,2], Tânia C. S. Pires[1,2], Irene Mediavilla[3], Luis Saúl Esteban[3], Isabel C.F.R. Ferreira[1,2], Sandrina A. Heleno[1,2], Lillian Barros[1,2*]

[1]Centro de Investigação Montanha (CIMO), Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[3]CEDER-CIEMAT, Autovia de Navarra A-15, Salida 56, 42290 Lubia, Spain
**lillian@ipb.pt*

As espécies *C. sempervirens* L. e *J. communis* L. são amplamente plantadas como arbustos ornamentais em parques e jardins, enquanto *C. ladanifer* L. é frequentemente encontrada em áreas silvestres. No entanto, estas espécies apresentam um elevado potencial para serem cultivadas em terrenos marginais [1]. Diferentes estudos investigaram a composição química dessas espécies por GC-MS; no entanto, a maioria refere-se ao óleo esencial (OE) obtido por hidrodestilação das folhas de *C. ladanifer* e *C. sempervirens*, assim como de bagas de *J. communis*, sendo escassa a informação sobre outras partes das plantas [2,3].

No âmbito do projeto BBI-JU BeonNAT, o presente estudo teve como objetivo avaliar a composição química de OE extraídos por destilação a vapor da parte aérea dessas três espécies e as suas propriedades bioativas (antioxidante, antibacteriana, citotóxica e anti-inflamatória) tendo como finalidade o desenvolvimento de produtos de base biológica em diferentes indústrias.

Assim, cada espécie foi colhida em duas origens diferentes para procurar diferentes quimiotipos associados a diferentes localizações geográficas [4]. Os resultados obtidos sugerem que a colheita dessas espécies em diferentes localizações geográficas interfere no rendimento do OE e respectiva composição química, sendo que o maior teor de terpenos foi observado em *C. sempervirens* seguido de *J. communis*. Com exceção de uma das origens de *C. ladanifer* que apresentou viridiflorol como o composto mais abundante, as três espécies apresentaram em comum o α-pineno como composto majoritário. Os OEs de *C. ladanifer* apresentaram potencial antibacteriano, apresentando valores de concentração mínima inibitória (CMI) de 0.3 a 1.25 mg/mL. Relativamente às restantes bioatividades, o OE de *C. ladanifer,* revelou uma inibição da oxidação de 83%, enquanto que o OE de *J. communis* apresentou citotoxicidade na linhagem celular MCF-7, e os OEs *C. sempervirens* e *C. ladanifer* exibiram o maior potencial na linha celular NCI-H460. Qualquer um dos óleos apresentou actividade anti-inflamatória, destacando-se o maior potential na especie de *C. sempervirens* (IC_{50}: 11-14 μg/mL), seguido do OE de *C. ladanifer (*IC_{50}: 19-21 μg/mL*)* e *J. communis* (IC_{50}: 24-85 μg/mL). As espécies avaliadas revelaram ser uma fonte viável e de baixo custo de OEs que podem ser utilizados para o desenvolvimento de produtos de base biológica em diferentes industrias.

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Semi-preparative separation and racemization study of MDPV enantiomers by liquid chromatography and absorption study on Caco-2 model

Ana Sofia Almeida[1,2,3,4*], Bárbara Silva[3,4], Sara Cravo[1,2], Fernando Remião[3,4], Carla Fernandes[1,2]

[1] Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto
[2] Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto
[3] UCIBIO – Applied Molecular Biosciences Unit, REQUIMTE, laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto
[4] Associate Laboratory i4HB - Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto
**Email: anasofiaalmeida1998@gmail.com*

Synthetic cathinones, such as 3,4-methylenedioxypyrovalerone (MDPV), are widely abused due to their psychostimulant effects [1]. Being chiral compounds, studying the influence of stereochemistry in their biological/toxicological properties (enantioselectivity) is of great importance [2,3] as well as the racemization phenomena since enantiomers can undergo racemization in certain temperature and acidic/basic environments [4]. Moreover, enantioresolution methods that allow the separation of the enantiomers of synthetic cathinones have been reported, being liquid chromatography (LC) using chiral stationary phases (CSPs) the technique of choice [5].

In this work, the semi-preparative enantioresolution of MDPV and a racemization study were performed by LC using amylose-derived CSPs. The enantiomers were successfully separated with a selectivity factor of 1.4 and a resolution factor of 1.7, collected with enantiomeric ratios (e.r.) higher than 95% and recovery rates of 92% and 93%. The racemization of the enantiomers of MDPV was affected by higher temperatures. Nonetheless, for 48 h at room temperature and 24 h at 37 ºC, the enantiomers were stable since minor/no changes were observed in the e.r. values.

Additionally, a permeability study was performed to evaluate the potential enantioselectivity of MDPV in the passage across the Caco-2 monolayer, a widely used *in vitro* model for intestinal permeability studies. To detect and quantify MDPV, an UHPLC method was developed and validated. High selectivity for MDPV and good linearity were observed in the tested concentration range (0.5-500 µM) with correlation coefficients always higher than 0.999. An accuracy ranging between 102 and 109%, inter-day and intra-day precisions with coefficients of variation below 15%, limits of detection and quantification of 0.063 µM and 0.19 µM, respectively, were also found. No statistically significant differences were found between the enantiomers in the passage across the Caco-2 monolayer (no enantioselectivity).

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QA13

Continuous flow bioconjugation of a fluorescent coumarin-lipid probe as a chemical reporter for membrane oxidation

Pedro A. M. M. Varandas[1,*], Ricardo L. Belinha[1], Sara S. Marques[1], Alexander J. A. Cobb[2], Vanda Vaz Serra[3], Marcela A. Segundo[1] Eduarda M. P. Silva[1,4]

[1]LAQV, REQUIMTE, Department of Chemistry Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2]Department of Chemistry, King's College London, 7 Trinity Street, London SE1 1DB, United Kingdom
[3]Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[4]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, Advanced Polytechnic and University Cooperative (CESPU), CRL, 4585-116 Gandra, Portugal
**pedrovarandas@hotmail.com*

Lipids are responsible for critical roles in many vital biological pathways. These biomolecules act as potent signalling agents since many diseases are associated with disruptions in lipid metabolism and function including neurological disorders, autoimmune diseases, and cancer [1,2]. Fluorescent labelling is one of the main tools used for the investigation of biological functions involving lipids, namely for clarifying metabolic pathways and molecular mechanisms of diseases where these molecules are of crucial importance [3]. In this work, an automated flow procedure was developed for the bioconjugation of a coumarin to a phospholipid, allowing to tailor the most suitable conditions for the synthesis of fluorophores covalently conjugated to these biologically relevant targets. The coumarin moiety (COUM) was chosen to provide a fluorescent-tag suitable for biological monitoring with low interference with the phospholipids structure and biological functions [4]. Moreover, a phosphatidylethanolamine derivative (POPE) was used since it belongs to one of the most abundant class of phospholipids in mammalian cells with an essential role in several cellular processes [5,6]. The possibility of using the coumarin-lipid probe to report the radical species attack to membranes was assessed by incorporating the probe in large unilamellar vesicles (LUVs) and multilamellar vesicles (MLVs) that were then exposed to oxidative conditions. The capacity of the COUM-POPE probe to report oxidation by AAPH-generated peroxyl radicals in egg L-α-phosphatidylcholine (EPC) vesicles was evaluated.

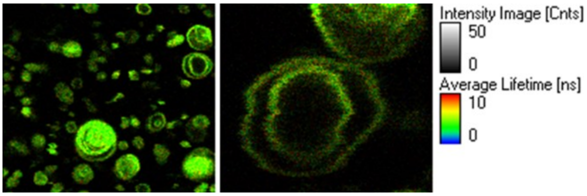

Fig. 1. FLIM images of MLVs incorporated with coumarin-POPE probe, (A) 80 mm^2; (B) 18 mm^2.

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Determinação cinética do ácido acetilsalicílico usando pontos quânticos de CdTe e de $AgInS_2$ como sondas fluorescentes e U-PLS e ANN como ferramentas quimiométricas

Rafael C. Castro[1*], Ricardo N.M.J. Páscoa[1], M. Lúcia M. F. S. Saraiva[1], David S.M. Ribeiro[1], João L.M. Santos[1]

[1] LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy,
University of Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal
**rafael.castro.cl@hotmail.com*

O ácido acetilsalicílico (AAS) é um dos medicamentos mais utilizados em todo o mundo, e uma das moléculas mais estudadas. O mecanismo de ação deste fármaco é dependente da dose, pelo que, para níveis de concentração baixos, é usado como agente anti-trombótico, na prevenção de doenças cardiovasculares. Por outro lado, para doses intermediárias e altas podem destacar-se os efeitos anti-inflamatório, analgésico e antipirético [1]. Mais recentemente, outros usos clínicos têm sido investigados, nomeadamente a sua atividade anti tumoral e o seu impacto na doença de Alzheimer [2,3]. O AAS tanto pode ser usado como único princípio ativo numa formulação farmacêutico, ou em combinação com outros princípios ativos de forma a melhorar a sua ação terapêutica [1].

Dentro das nanopartículas fluorescentes usadas em química analítica, os pontos quânticos têm-se destacado devido às suas propriedades óticas e químicas muito interessantes. Entre muitas características fascinantes podem destacar-se a facilidade de adaptação da sua síntese em função das características do nanomaterial que se pretende obter, o ajuste da sua química de superfície que permite modular a sua reatividade e o facto de possuírem um espectro de absorção amplo ao passo que o seu espectro de emissão é estreito, possibilitando a excitação simultânea de vários QDs numa única sonda combinada usando apenas um único comprimento de onda de excitação [4,5].

A baixa seletividade tem sido destacada como a principal desvantagem do uso destes nanomateriais em química analítica, especialmente em amostras complexas. Assim, algumas estratégias têm sido desenvolvidas com vista a resolver este problema, sendo que o uso de ferramentas quimiométricas para tratar os dados de fluorescência obtidos tem sido um dos que mais se tem destacado [4]. O uso de dados de segunda ou maior ordem (como por exemplo dados cinéticos ou matrizes de excitação-emissão - EEM) quando acoplados a ferramentas quimiométricas adequadas possibilitam determinar o analito mesmo na presença de espécies interferentes não incluídas durante a calibração.

Neste trabalho pontos quânticos binários de CdTe e ternários de $AgInS_2$ foram combinados numa única nanossonda para determinar AAS em formulações farmacêuticas. Os dados cinéticos foram processados por diferentes ferramentas quimiométricas, nomeadamente *unfolded-PLS* (U-PLS) e *artificial neural network* (ANN). A ferramenta quimiométrica com que qual se obteve dados mais robustos possibilitou a quantificação de AAS, mesmo na presença de outros princípios ativos.

Agradecimentos

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Development of a new mesofluidic platform to assess metal-based dihydrofolate reductase inhibitors

Sarah A. P. Pereira[1, *], Lorenzo Biancalana[2], Fabio Marchetti[2], Paul J. Dyson[3], M. Lúcia M. F. S. Saraiva[1]

[1] REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira, nº 228, 4050-313 Porto, Portugal.
[2] Dipartimento di Chimica e Chimica Industriale Università di Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy
[3] Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland
**sarah.pp@hotmail.com*

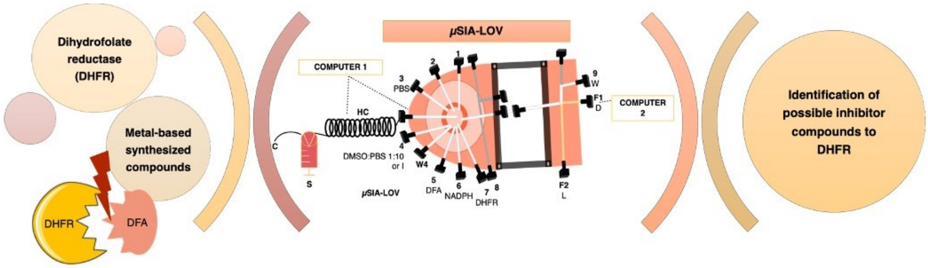
A new versatile, robust, rapid, and miniaturized micro sequential injection coupled with the lab-on-valve (µSIA–LOV) technique was full-blown to perform inhibitory studies on the dihydrofolate reductase (DHFR) enzyme using metal-based compounds (Fig. 1).

DHFR catalyzes the reduction of dihydrofolate to tetrahydrofolate in an NADPH-dependent manner [1]. This enzymatic reaction interferes with the various amino acids, thymidylate, and purines biosynthesis and is also an important target for anticancer drugs such as methotrexate [2]. Ruthenium and diiron compounds have been extensively studied *in vitro* and *in vivo* since they are showing promising anticancer properties [3,4].

The metal complexes exhibited IC_{50} values in the range 1.3 ± 0.3 to 108 ± 7 µM, with half of the complexes lying in the low µM range, i.e., 1.3 ± 0.3 to 4.4 ± 0.2 µM. For comparison, methotrexate (MTX), a known inhibitor of DHFR, has an IC_{50} value of 0.38 ± 0.06 µM.

The automated system requires very little sample (approximately 40 µL per analysis), uses minimal reagents (5 times less than the batch procedure used), and generates very little waste (around 1.2 mL per analysis) compared with batch methods, considerably reducing costs.

Fig.1 - µSIA-LOV developed system used to identify possible metal-based inhibitors for DHFR enzyme.



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Estudio fluorescente de la amina biógena Triptamina y su aminoácido precursor (Triptófano).

Mora-Diez, N.[*], **Rodríguez-Cáceres, M.I., García-Escobar, E.**

Departamento de Química Analítica e Instituto de Investigación del Agua,
Cambio Climático y Sostenibilidad (IACYS)
Av. Elvas s/n, 06006 Badajoz, España.
**nielene@unex.es*

Las aminas biógenas provienen de la descarboxilación enzimática de aminoácidos [1]. Grandes cantidades de aminas biógenas producen efectos tóxicos en nuestro organismo [2]. Además de encontrarse en los organismos vivos, ellas se pueden encontrar en alimentos y bebidas fermentadas. Se generan durante un inadecuado procesamiento o almacenamiento, como consecuencia de la actividad microbiológica. Por esta razón, su detección y cuantificación es esencial en el control de la calidad de los alimentos. El objetivo de este trabajo ha sido el estudio espectrofluorimétrico de la amina biógena Triptamina y su precursor, el aminoácido Triptófano.

Ambos analitos fueron estudiados por fluorescencia molecular, encontrándose que la señal de fluorescencia de la Triptamina es más intensa que la de su precursor. Durante la optimización de los parámetros instrumentales y químicos tales como el pH y la presencia de ciclodextrinas, surfactantes e iones metálicos, se vió que el Cu^{2+} a valores mayores de 50 ppm hacía que la señal del Triptófano desapareciera, mientras que no afectaba prácticamente a la señal de la Triptamina.

Se ha explorado la posibilidad de determinar Triptamina en presencia de Triptófano. Se estudió la variación de la señal de fluorescencia en ambos analitos en función del pH y en presencia de Cu^{2+} para encontrar las condiciones óptimas. Se observó que la señal de Triptamina + Cu^{2+} es máxima en medio ácido, mientras que la señal del Triptófano en presencia de este ión metálico desaparece por encima de pH 7. De esta forma, existe la posibilidad de determinar Triptamina en presencia de su aminoácido precursor, el Triptófano.

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Validation of a method to quantify essential and potentially toxic elements in raw and cooked food matrices

Nicole Ferreira[1,*], **Bruno Henriques**[1], **Thainara Viana**[1], **Lina Carvalho**[2], **João Pinto**[1], **João Colónia**[1], **Eduarda Pereira**[1]

[1]Departament of Chemistry, LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal
[2]Central Laboratory of Analysis, University of Aveiro, 3810-193 Aveiro, Portugal
*nicoleviana@ua.pt

Food contains minerals, which are required by the organism in small amounts and are essential for regulating metabolism and maintaining human health. However, it can also be a source of potentially toxic elements (PTEs), *i.e.* Hg, As, Cd, non-essential elements with potential hazardous effects on living organisms and ecosystems, even in low concentration [1]. Whether for nutritional research, risk assessment or compliance with food legislation, analytical methods that allow easy, fast, accurate and reliable determination of multiple elements simultaneously are essential. Those methods should be validated against specified performance criteria (e.g., linearity, specificity, precision, limits of detection and quantification, repeatability) to guarantee the quality of the results [2]. Many methods for quantifying minerals and PTEs in food are described in the literature, which make it difficult to choose the most appropriate method, once some focus exclusively on one group of elements or imply the use of different quantification techniques to determine the set of different elements groups. Most studies are only validated for a single food matrix (e.g., rice or fish or chicken, etc) and authors often do not specify whether the food has been processed or not.

The present work aimed to validate a simple and efficient method that can be used routinely and guarantees the correct and simultaneous determination of the concentrations of macro-, and micro-minerals, and PTEs in different real food matrices (raw or processed state). As the effects of processing/cooking on food compositional values are not yet well described and understood, it was also examined whether different food processing (grilled and boiled) could alter the mineral and PTEs content of the foods studied. Based on the results, recommended intakes of the foods studied were proposed according to the Recommended Dietary Allowance and the Tolerable Upper Intake Level [3].

A single digestion method, based on HNO_3 and H_2O_2 in conjunction with microwave (elevated temperature and pressure) was applied to various real food matrices (fish, chicken, mussels, rice, and seaweed) to decompose the samples and solubilize macro, micro, and potentially toxic elements. The elements were then quantified by inductively coupled plasma mass spectrometry (ICP-MS).

The performance of the method met the requirements of the Portuguese Association of Accredited Laboratories (RELACRE), being successfully validated for As, Ca, Cd, Cu, Fe, Mg, Mn, Na, and Zn, for certified reference materials and real food samples. The blank (with values < LOD), fortification samples (percentages of recovery always between 80-120%), certified reference material (bias < 10%), and food samples results met the performance requirements defined by RELACRE.

Results showed that cooking food samples (boiled, or grilled) lead to significant changes (p-value < 0.05) in the concentration of most of the elements, although no significant changes were seen between treatments. For example, Na content in raw fish was reduced from 53.6 to 0.003 mg/g in boiled and grilled fish, reducing the health concerns associated with the ingestion of this element (100 g of raw fish, consumed typically in Japanese cuisine – shusi - would surpass 2.3 times Na recommended dose). Estimations of the amounts to be consumed to reach the recommended daily doses were attained for all minerals studied.

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In vitro inhalation bioaccessibility estimation of atmospheric PM-associated organic compounds using simulated biological fluids

J. Sánchez-Piñero[1,*], N. Novo-Quiza[1], J. Moreda-Piñeiro[1], S. Muniategui-Lorenzo[1] and P. López-Mahía[1]

[1]University of A Coruña. Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Department of Chemistry. Faculty of Sciences. Campus de A Coruña, s/n. 15071 – A Coruña. Spain.
**joel.sanchez@udc.es*

According to the World Health Organization (WHO), ambient air pollution is estimated to cause up to 9 million deaths annually and millions of lost years of healthy life worldwide [1]. Among air pollutants, atmospheric particulate matter (PM) was classified as carcinogenic to humans and several epidemiologic studies have associated PM inhalation to specific adverse health outcomes. Their toxicity is mostly attributed to particle size (being PM_{10} and $PM_{2.5}$ the most studied fractions due to their potential to penetrate and deposit in different regions of respiratory system after inhalation) and to PM-associated pollutants (potential contributors to PM toxicity) [2]. As posing a great risk, several countries have implemented limit values and emission reduction measures to minimize the risk, which are currently based on the total pollutant content in PM. In the last decades, studies have been focused on the determination of the pollutant fraction that can be dissolved in respiratory fluids (inhalation bioaccessibility) as they could provide valuable information of how substances may interact with organisms. In addition, bioaccessibilities are considered better estimators of the health risk posed by pollutants against the overestimation when total concentrations are used, being broadly used in human health risk assessment models to achieve a more realistic assessment [3]. Different methods have been performed to estimate inhalation bioaccessibilities of substances, being *in vitro* physiologically based extraction tests (PBET) the most preferred alternative due to their benefits. These tests involve the use of simulated biological fluids for extracting PM pollutants (i.e., bioaccessible fraction) under conditions (temperature, agitation, solid-liquid ratio (S/L) and extraction time) similar to those found in the human body. Moreover, the use of controlled conditions to perform the tests allow the study of parameters influencing bioaccessibilities [4].

In this work, the study of inhalation bioaccessibility of pollutants associated to PM by an *in vitro* PBET approach was performed, using Gamble’s and artificial lysosomal fluid (ALF) solutions as simulated fluids as being representative of different lung regions. Due to the lack of standardized PBET conditions, they were selected basing on the available literature to obtain the most realistic results, while validated analytical procedures for the measurement of pollutants occurring in PM and bioaccessible fractions were applied. Bioaccessibilities of 23 % and 31 % were estimated by average for polycyclic aromatic hydrocarbons (PAHs) in PM_{10} and $PM_{2.5}$, respectively; while mean bioaccessibilities of 83 %, 68 % and 41 % were obtained for bisphenol A, organophosphorus flame retardants (OPFRs) and phthalate esters (PAEs), respectively, in $PM_{2.5}$. Also, correlations between bioaccessible ratios and PM properties were observed (mainly with $PM_{2.5}$ carbon content), while health risk assessment considering both total and bioaccessible pollutants’ concentrations was conducted.

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Automatic identification of myeloperoxidase natural inhibitors in plant extracts

Fátima A. R. Mota[1*], Sarah A. P. Pereira[1], André R. T. S. Araújo[1,2], Beatriz Gullón[3], Marieta L. C. Passos[1], M. Lúcia M. F. S. Saraiva[1]

[1] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, Porto University, Rua Jorge Viterbo Ferreira, No. 228, 4050-313 Porto, Portugal;
[2] Unidade de Investigação para o Desenvolvimento do Interior, Instituto Politécnico da Guarda, Avenida Dr.Francisco de Sá Carneiro, No 50, 6300-559 Guarda, Portugal;
[3] Department of Chemical Engineering, Faculty of Science, Universidade de Vigo (Campus Ourense), As Lagoas, 32004 Ourense, Spain;
fatimaamota@gmail.com

The aim of this study is to assess the action of different plant extracts on the activity of enzyme myeloperoxidase (MPO) in an automatic way. As promising candidates for MPO inhibition, it is intended to understand how the constituents of these extracts correlate with their antioxidant and anti-inflammatory properties.

In inflammatory and infectious processes, the concentrations of this enzyme are increased, being an inhibition target to limit these processes [1].

For this, an automatic sequential injection analysis (SIA) system was developed and optimized, and the results showed very satisfactory accuracy and precision.

In the group of selected plant extracts, IC50 values from 0.029 ± 0.002 mg / mL to 35.4 ± 3.5 mg / mL were obtained. Arbustus Unedo proved to be the most inhibitory extract for MPO based on its phenolic

compound content.

Considering the simplicity and speed of the automatic SIA method, its coupling to MPO inhibition assays becomes a good alternative to other conventionally used methods.

This work also supports the pharmacological use of these species that may be related to the treatment of infection and inflammation [2].

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As vantagens do uso da quimiometria na química analítica

Ricardo N.M.J. Páscoa[*], **Rafael C. Castro, João L.M. Santos, David S.M. Ribeiro**

LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy,
University of Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal
*rnpascoa@ff.up.pt

A quimiometria consiste no uso de métodos matemáticos e estatísticos multivariados para otimização de desenhos experimentais, para melhorar a compreensão dos dados físico/químicos obtidos pelos métodos de referência e para correlacionar as propriedades físico/químicas de amostras com os dados instrumentais. Nesse sentido, esta disciplina não pretende retirar protagonismo aos métodos de referência ou técnicas experimentais comummente utilizadas (pois sem estes torna-se menos abrangente) mas sim funcionar como uma ferramenta completar.

Os métodos matemáticos/estatísticos multivariados possuem diversas vantagens em relação aos métodos univariados. A primeira grande vantagem que pode ser enumerada está relacionada com a presença de interferentes nas amostras. Nos métodos univariados onde apenas um valor/ponto é medido por cada amostra (dados considerados de ordem zero), é fácil perceber que se as amostras possuírem um interferente, o valor/ponto registado pode ser afetado pela presença deste interferente. Esta situação acarreta normalmente diversas operações um pouco complexas (ex: filtração, derivatização, separação, etc) para a remoção do mesmo, tornando o método menos simples, mais moroso, dispendioso e geralmente menos amigo do ambiente. Em relação aos métodos multivariados onde vários valores/pontos são medidos na mesma amostra (dados considerados de primeira, segunda, etc ordem dependendo do ou dos equipamentos utilizados) a presença de um ou mais interferentes nas amostras não é muito relevante, pois o efeito destes na quantificação do analito de interesse pode ser evitado através da aplicação das ferramentas quimiométricas corretas. Por exemplo, se estivermos a lidar com dados de primeira ordem (vector de dados, ex: espectro de infravermelho próximo) basta que o conjunto de amostras utlizadas na calibração contenham a presença do interferente para ser possível determinar o analito de interesse em amostras não calibradas. No entanto, se estivermos a lidar com dados de segunda ordem (matriz de dados, ex: espectros de infravermelho próximo recolhidos ao longo de um período de tempo), não é necessário utilizar amostras na calibração que contenham a presença do interferente para ser possível determinar o analito de interesse em amostras com interferentes não calibrados. Isto é, é possível quantificar o analito de interesse em amostras de validação que contenham um ou mais interferentes que não foram introduzidos na etapa de calibração devido à conhecida vantagem de dados de segunda ordem. Outra grande vantagem da utilização dos métodos matemáticos/estatísticos em relação aos métodos univariados é a capacidade que estes possuem para realizarem determinações multiparamétricas através de uma única análise. Isto deve-se à aquisição de vários valores/pontos como referido anteriormente que podem conter informação de vários analitos (ex: espectro infravermelho-próximo). Outras vantagens que podem ser referidas são o aumento da seletividade, sensibilidade, bem como a identificação de outliers [1,2,3].

Assim, a utilização da quimiometria é uma ferramenta importante de apoio à química analítica e o seu uso é cada vez mais indispensável em diversas áreas.

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Low pressure chromatographic system with multiple pulse amperometric detection for multi-analyte determination in green coffee extracts

Alexandra Rangel Silva[*], **João Rodrigo Santos, P. J. Almeida, J. A. Rodrigues**

Faculdade de Ciências da Universidade do Porto, rua do Campo Alegre s/n, 4169–007, Porto, Portugal
**up201504466@fc.up.pt*

Short-length monolithic column in low pressure flow systems is a recent approach of high analytical potential. This strategy combines the use of a monolithic column (able/known of high separation efficiency) and the versatility of FIA systems, to enable the implementation of miniaturized chromatographic systems with different tailored valences [1-3].

In recent works, a low pressure chromatographic system with an amperometric detector was used for the determination of trigonelline at cathodic potentials [1], and caffeine and chlorogenic acids at anodic potentials [2]. In this work, the simultaneous determination of these analytes in green coffee extracts was performed. To this goal, one exploited the electrochemical technique multiple pulse amperometry, which has been scarcely used in analytical approaches. The chromatographic system was based on a 1 cm-length C_{18} monolithic column and an amperometric detector comprising a boron-doped diamond working electrode, an AgCl/Ag reference electrode and a glassy carbon auxiliary electrode. The separation of the compounds was achieved through ion-pair chromatography.

The following experimental conditions were evaluated: the mobile phase composition, the supporting electrolyte composition for the electrochemical detection and the potential conditions inherent to the multiple pulse amperometry technique. The developed methodology allowed the simultaneous separation and identification of 4 antioxidant compounds in green coffee extracts: trigonelline, 5-caffeoylquinic acid, caffeine and 5-feruloylquinic acid (Figure 1). The developed methodology presented a determination rate of 9 analyses *per* hour, an eluent consumption of 5 mL *per* analysis and a detection limit of 17.6 $\mu mol.dm^{-3}$, 11.8 $\mu mol.dm^{-3}$ and 10.3 $\mu mol.dm^{-3}$ for trigonelline, 5-CQA and caffeine, respectively.

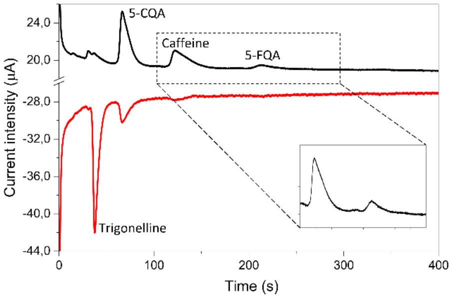

Fig.1. Chromatogram obtained at the optimized conditions of mobile phase composition and detection parameters. Applied potentials: — +1.6 V (0.03 s); — -1.5 V (0.03 s).

Acknowledgements
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QA22

Quantitative analysis of phosphopeptide enrichment methods

Gonçalo Martins[1], José L. Capelo[1,2], Carlos Lodeiro[1,2], Hugo M. Santos[1,2] *

[1]BIOSCOPE Research Group, Department of Chemistry, LAQV-REQUIMTE, Faculty of Sciences and Technology.
Universidade NOVA de Lisboa, 2829-516 Caparica – Portugal
[2]PROTEOMASS Scientific Society, Madan Parque, Building VI, Office 23, Faculty of Sciences and Technology, 2829-516, Caparica – Portugal
**hmsantos@fct.unl.pt*

Protein phosphorylation plays a significant role in many biological mechanisms, including cell differentiation, cell cycle control, metabolism, and apoptosis, therefore, being systematically associated with several diseases such as cancer and neurodegeneration. Enrichment is a crucial procedure step to overcome analytical challenges related to the nature of phosphoproteins, such as their dynamic modification patterns, sub-stoichiometric concentrations, and low mass spectrometric response. [1]

Ion metal affinity chromatography (IMAC) has become the most used among the several phosphopeptide affinity enrichment techniques. Despite continuous developments of IMAC materials for phosphopeptide enrichment, unbiased and quantitative recovery of phosphopeptides in complex biological mixtures continues to pose a challenge. For example, the peptides' aminoacidic composition significantly impacts their affinity for the various metal ions used in IMACs. As a result, quantifying phosphopeptide content while retaining high selectivity remains difficult. [2]

In our work, we have compared three different methods for phosphopeptide enrichment (an in-house method that was optimized, a commercial kit (Thermo Scientific REF: A32993) and the EasyPhos protocol) [3] towards a typical. The in-house method has revealed the highest number of unique phosphosites compared to the other two methods. Despite this result, an ICP-MS analysis of the enrichment has shown only 40% of the phosphorous initially contained in the sample. Considering these results, ICP-MS analysis must be applied to the other methods. However, there is mass spectrometry evidence that they are underperforming methods. These findings should be taken into consideration when presenting quantitative phosphoproteomics findings.

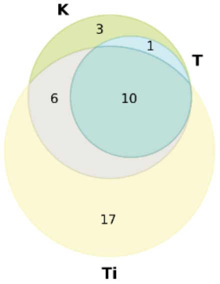

Fig.1. Venn's diagram of unique phosphopeptides identified by mass spectrometry for each method.
K: Thermo Scientific Kit; T: EasyPhos/Titansphere; Ti: In-house Ti-IMAC Protocol

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Overcoming the seawater trace elements analysis challenge in a SPE-flow-based approach

Tânia C. F. Ribas[*], **António O. S. S. Rangel**

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório
Associado, Escola Superior de Biotecnologia, Porto, Portugal
**tpedro@ucp.pt*

The determination of chemical species in the different environmental matrices presents different challenges depending on the sample nature (water, soil and plants). Water is vital for life in all aspects, not only for consume but also for recreational purposes, what makes its monitoring indispensable. The important chemical processes that alter water composition vary on the water source (groundwater, river, lake and seawater), consequently varying the expected concentration of the present species. Additionally, human activity can also interfere with water quality. So, in the analysis of different types of water, there are different challenges depending on the water source and the probable existing problems. The analytical tools should ideally be developed to assess any substances (changed element content and/or element contamination) that may interfere with water quality and consequently with life [1]. Regarding seawater and its intrinsic characteristics (matrix composition and the usually trace analyte concentration) makes its monitoring an extra challenge. Some strategies can be employed to overcome the encountered challenges, being one of them solid phase extraction (SPE).

SPE is a sample pre-treatment extensively used in analytical chemistry. It is a versatile technique in sample preparation for sample matrix removal and/or analyte enrichment, making it appealing to apply to the seawater monitoring. The principle of SPE is based on the partitioning of solutes between two different phases. This process occurs between a liquid phase (usually the sample matrix) and a solid phase (the sorbent material). This way, it enables the enrichment of the target analyte and/or clean-up of the sample matrix, thus favouring the analytical process [2]. This sample preparation technique can easily be coupled with a variety of other techniques used in analytical chemistry such as flow-based methods (flow injection and sequential injection analysis). Flow-based methods are appealing to implement this type of strategy for the in-line sample preparation due to the associated apparatus versatility. The high versatility of a SPE strategy makes it fairly easily to be implemented into a flow-based manifold, as well.

When the two techniques are coupled, flow-based methods with SPE, the system gains the inherent advantages of the two techniques: (i) the automation and miniaturization of the sample extraction, in a flow-based mode; (ii) decrease the time needed per analysis, thus improving sample throughput; (iii) minimize the operator sample handling; (iv) improve the method precision and (v) minimize the overall reagents/sample consumption [3]. Some of these applications are discussed in this communication.

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Finding biomarkers of ruminal acidosis through targeted and untargeted metabolomic analysis through *in vitro* rumen fermentation assays

Inês M. Valente[1,2]*, Liliana Cordeiro[1], Margarida R. G. Maia[1], Hugo M. Oliveira[3], José A. Rodrigues[2], António J. M. Fonseca[1], Ana R. J. Cabrita[1]

[1]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2]REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
[3]INL, International Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga s/n, 4715-330 Braga, Portugal
**ines.valente@fc.up.pt*

Ruminal acidosis is a metabolic disease with a high incidence in intensive dairy farms, where high producing cows are fed diets with high inclusion of rapidly fermentable carbohydrates to meet their energy needs. Measurement of ruminal pH is considered the golden standard for acidosis diagnosis, but results are often conflicting. Although volatile fatty acids, particularly acetate and propionate, originating from the ruminal fermentation of feed are also often used as markers of rumen acidosis, information is lacking on the potential of minor compounds as reliable markers of this disorder. Quantitative metabolomic methods have opened new avenues to elucidate the associations of feeding and rumen health, being a useful approach to characterize metabolic disorders in dairy cows.

This work aimed the characterization of the fermentation media from *in vitro* batch incubations promoting acidotic conditions. For the study, rumen content collected from rumen-fistulated Holstein cows was incubated anaerobically at 39 ºC, for 12 h, with 5 experimental treatments containing carbohydrate sources of different fermentability: cellulose, corn starch, wheat starch, cellulose + corn starch (50:50, w/w), and cellulose + wheat starch (50:50, w/w). Every 4 h the incubation media was characterized in terms of fermentation parameters (pH, total gas and methane production, NH_3-N, and volatile fatty acids), the 12-h incubation media being submitted to targeted metabolomic (minor volatile compounds) analysis by gas chromatography with flame ionization detection (GC-FID) [1], and untargeted characterization by high performance liquid chromatography with high resolution tandem mass spectrometry (HPLC-MS/MS) analysis [2], in both positive and negative ionization modes.

Acidotic conditions ($pH < 5.8$) were achieved at 8 h in incubations with starch sources. After 12 h, incubations with pure starch and cellulose with starch resulted in the formation of the minor volatile compounds 3-methylbutanal, 3-methyl-2-pentanone, 2-hexanone, and 2-pentenal, which was not verified when pure cellulose was used as substrate. Also, the levels of these metabolites were significantly ($p < 0.05$) different between fermentation media from incubations with pure starch (corn and wheat starch) and those with 50% starch and 50% cellulose. The analysis of data by Partial Least Squares Discriminant Analysis (PLS-DA) showed a separation between 3 main groups of substrates (pure cellulose, pure starch, and mixed starch and cellulose). The main metabolites responsible for the discrimination between groups were obtained by the weighted sum of absolute regression coefficients, revealing higher levels of lactic acid, Leu-Ile, Val-Phe, and Ile-Leu in starch containing incubations. The metabolic pathways involved on the formation of the identified biomarkers of acidotic conditions by *in vitro* incubations is under investigation and will be discussed.

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Renewable immunosensors based on lab-on-valve flow systems

Sara S. Marques, Diana R. Cunha, Bruno J. R. Gregório, Sara R. Fernandes, Luisa Barreiros, M. Beatriz Quinaz, Marcela A. Segundo*

LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-213 Porto, Portugal.
**msegundo@ff.up.pt*

Flow-based methods have been developed over the last few decades to automate (bio)chemical analysis while improving the figures of merit regarding accuracy, precision and sample throughput. Several generations of flow analysers have been proposed [1, 2], including the lab-on-valve (LOV) flow systems. Considered as the third generation of Flow Injection Analysis (FIA), LOV is based on a monolithic structure with microconduits machined in a polymeric block, mounted atop a multiposition selection valve [3]. Due to the mesofluidic scale of these channels, this technique presents more potential and compatibility with real-world samples when compared to microfluidic devices, namely on the implementation of renewable solid-phase (bio)chemistry. In this context, immunosensors offer the selectivity and low detection limits required by current analytical challenges. However, reproducibility issues are often pointed out as an important drawback as well as the limited reuse due to permanent binding of analytes and/or interferents to the biorecognition element.

In the present work, a versatile LOV-based flow system is proposed for the automation of construction and operation of immunosensors. Using Sepharose microbeads decorated with protein A, an automated protocol for the retention and immobilization of this solid-phase in a flow-through detection cell was devised. The flow cell was established within the LOV channels, defined by two optical fibres (600 µm), one connected to a UV-Vis light source and the other to a UV-Vis CCD spectrometer, with a flow restriction element in the vertical outlet. This design allowed the in-situ construction of the immunosensor, with monitoring of all on-column events, including antibody immobilization, interaction of the immunorecognition element with the (bio)analytes in sample, the surface regeneration and/or the solid-phase discard. The proof of concept was established for the quantification of human immunoglobulin in human serum and saliva [4]. Application to challenges pertaining to pharmaceutical formulation are current under development, namely the quantification of nanoparticles in drug formulation and the evaluation of the amount of polyethylene glycol (PEG) in nanoformulations.

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Detetores baseados em imagem: desenvolvimento e aplicação

<u>Rui A.S.Lapa</u>, Sara C. Cunha, J. O Fernandes, João L.M. Santos, Rafael C. Castro, David S.M. Ribeiro

LAQV, REQUIMTE, Faculdade de Farmácia, Universidade do Porto
**ruilapa@ff.up.pt*

Nos últimos anos tem surgido uma nítida tendência no sentido do desenvolvimento e aplicação de sensores e detetores baseados em imagem (DIB), que tem vindo a ser amplamente estudado tendo como objetivo da sua aplicação analítica. Características como sejam a portabilidade, rapidez, fornecerem resultados precisos e exatos, além da boa relação custo-benefício justificam essa tendência, devido principalmente ao facto dos DIB permitirem implementar dispositivos para realizar análises in situ, a que se associa o baixo consumo de reagentes e a concomitante redução de resíduos.

Basicamente os DIB baseiam-se na captura de imagem obtidas após reações colorimétricas ou luminescentes, sendo essa imagem convertida em dados segundo algoritmos usuais de análise de imagem, permitindo correlacionar cores com a concentração do analito.

Para realizar a captura de imagem podem ser usados diversos dispositivos como câmaras CCD e CMOS, digitalizadores ou mesmo câmaras de telefones móveis.

Dado que a captura de imagens necessita de condições estáticas, é necessário recorrer a plataformas de suporte para o sistema químico, normalmente contidos em placas de reação ou mais frequentemente microplacas de poliestireno. Essas plataformas podem ser construidas por peças previamente recortadas ou através de impressão 3D. Sempre que há necessidade de incluir uma fonte de excitação, como é o caso da espectrofluorimetria, instalam-se na plataforma os emissores adequados, usualmente LEDs, tubos de descarga ou fontes de filamento.

O detetor fluorimétrico (DIB) desenvolvido foi aplicado na quantificação de histamina usando a redução de fluorescência promovida por pontos quânticos. Com esse objetivo foi necessário a criação de uma plataforma que incluísse a fonte de luz UV, um dispositivo de captação de imagem (Cãmara CMOS) características de resolução e sensibilidade adequadas e adaptação de software (baseado em ImageJ) de forma a realizar o tratamento das imagens e a obtenção de dados com possibilidade de tratamento numérico de forma fácil. Todo o conjunto é de pequena dimensões, portátil e de baixo custo.

A plataforma foi construída em poliestireno e acrílico, tendo as diferentes partes sido desenhada em CAD e cortadas com um dispositivo CAM. Finalmente foram montadas de forma a constituir uma câmara de leitura que pudesse incorporar a fonte de luz e o detetor. A fonte de radiação UV utilizada consistiu em LEDs UV de 365 nm ou lâmpadas de descarga de baixa potência.

Os resultados obtidos com o dispositivo DIB desenvolvido na quantificação de histamina adequada e significativamente com os obtidos por metodologias envolvendo a utilização de detetrores fluorimétricos convencionais.

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QUÍMICA-FÍSICA

Development of Chemiluminescent Halogenated Coelenterazine Derivatives with Anticancer Potential

Luís Pinto da Silva[1,*], Carla M. Magalhães[1], Patricia González-Berdullas[1], José E. Rodríguez-Borges[2], and Joaquim Esteves da Silva[1]

[1]Centro de Investigação em Química (CIQUP), Instituto de Ciências Moleculares (IMS), Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
**luis.silva@fc.up.pt*

Photodynamic therapy (PDT) is an anticancer treatment with several advantageous characteristics, such as few side-effects and a minimally invasive nature. More specifically, PDT consists in the administration to the patient of a photosensitizer (PS) that is activated by light-irradiation of the tumor site, leading to production of the highly cytotoxic singlet oxygen. However, light has a low penetration depth into biologic tissues, making this treatment mainly suitable for the treatment of surface tumors. Herein, we developed new single-molecule PSs based on the marine chemiluminescent (CL) species, Coelenterazine. CL consists in the conversion of thermal energy into excitation energy, due to a chemical reaction without light-irradiation [1,2]. Based on this species, new halogenated derivatives were developed, which are capable of intracellular self-activation by undergoing a CL reaction triggered by a cancer marker [3-6]. More specifically, these Coelenterazine-based PSs are chemiexcited directly to triplet excited states capable of sensitizing the highly cytotoxic singlet oxygen, without the need for an external light source [3-6].

In vitro cytotoxicity assays revealed that these derivatives showed anticancer activity toward several cancer cell lines, without the need for light-irradiation, with some of them showing activities comparable with reference chemotherapeutic drugs [3-6]. More relevantly, the proposed derivatives did not show toxicity toward noncancer cells, demonstrating an interesting profile of tumor-selectivity [3-6]. Thus, these studies show that halogenated Coelenterazine derivatives have potential to be used as a basis for novel light-free PDT modalities.

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Probucol – solvent effects on polymorph crystallization

João A. Baptista[1,*], Mário T. S. Rosado[1], Ricardo A. E. Castro[2], João Canotilho[2], Elvira Fantechi[3], Laura Chelazzi[3], Samuele Ciattini[3], M. Ermelinda S. Eusébio[1]

[1] Coimbra Chemistry Center -Institute of Molecular Science, University of Coimbra, Portugal
[2] Faculty of Pharmacy, University of Coimbra, Portugal
[3] Centro di Cristallografia Strutturale, Università degli Studi Firenze, Italy
**jabaptista@qui.uc.pt*

The lack of control of the polymorphic form of active pharmaceutical ingredients (API) may have undesirable consequences on their manufacture and biological performance. Therefore, polymorph identification and selectivity of their preparation are crucial factors in API development. Crystallization from solutions is widely used in the industry, in the final steps of API synthesis and purification. The polymorph obtained in these processes is often dependent on experimental conditions, particularly on the solvent which may influence both the API conformation and intermolecular association. Nevertheless, a comprehensive understanding of solvent effects on the polymorph output in a crystallization process remains a major challenge.[1]

In this study, an investigation of the solvent effect on crystallization of solid forms of the pharmaceutical drug probucol (PROB) was performed. PROB is an hyperlipidemic drug developed for the treatment of coronary disease. Its molecule has a high conformational flexibility and two hydroxyl groups that can interact trough hydrogen bonds. Two polymorphs with an enantiotropic relationship were previously characterized (I and II) with the presence of a third form noted. [2]

In this investigation, crystallization in different conditions gave rise to 6 new forms of PROB, 2 polymorphs (Fn1 and Fn2) and 4 solvates (two of them isostructural to form II), that were characterized using infrared spectroscopy, polarized light thermomicroscopy, differential scanning calorimetry and X-ray technics (powder and single crystal). The structural characterization of the solvates was an important step for the identification of intermediate species that give rise to polymorphs with less stable conformations. A computational investigation was initiated to try to rationalize the effect of the solvent on the formation of the different polymorphic forms.

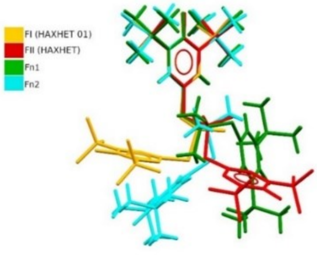

Fig.1. Conformations of PROB molecule in polymorphs FI, FII, Fn1 and Fn2.

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Active regulation of thermal transport using light-responsive molecular materials

N. Varela-Domínguez[1*], **C. López-Bueno**[1], **A. López-Moreno**[1,2], **G. Rama**[1], **V. Leborán**[1], **M. Giménez-López**[1], **F. Rivadulla**[1]

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, C/ Jenaro de la Fuente s/n, Santiago de Compostela, Spain.
[2]Present address: IMDEA Nanociencia, C/ Faraday 9, Madrid, Spain
*noavarela.dominguez@usc.es

Developing systems that can be switched between states with different thermal conductivities is one of the current challenges in materials science. Despite their enormous diversity and chemical richness, molecular materials have been only scarcely explored in this regard [1].

Here we report the synthesis and thermal conductivity [2] of 4,4'-dialkyloxy-3-methylazobenzene derivatives with different alkyl chain lengths [3, 4], allowing thermal conductivity changes in a controllable manner. These systems show a rich thermal phase diagram, with different crystalline, anisotropic mesophases, and isotropic liquid configurations, as a function of temperature. We have measured the temperature dependance of the thermal conductivity across these phases, showing that the changes in the alignment of the alkyl chains result in a large and reversible change of the thermal conductivity, up to 30%. On the other hand, the conformational transition between trans-cis azobenzene groups under UV/Vis illumination leads to reversible changes of thermal conductivity up to 40%.

To increase the kinetics of the thermal conductivity switch, we dispersed low concentrations of azobenzene derivatives in room-temperature commercial liquid crystals. Using this approach, we achieved multiple thermal states, and a bi-directional switching of their thermal conductivity using UV/Vis illumination (Fig. 1).

Given the enormous variety of photoactive molecules and chemically compatible liquid crystal mesophases, this approach opens unforeseen possibilities to develop effective thermal switches based on molecular materials.

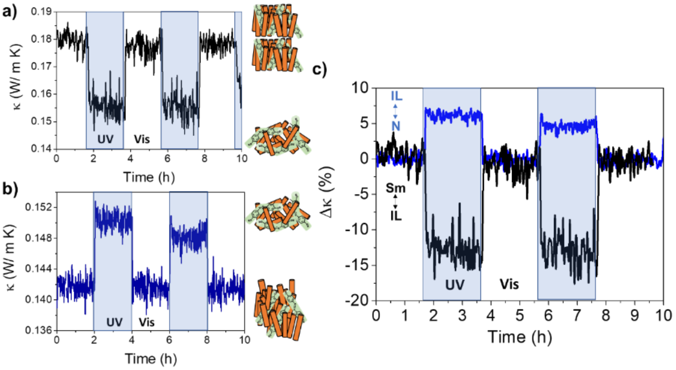

Fig.1. Doping the 4-octyl-4'-cyanobiphenyl liquid crystal matrix with 4% (w/w) of light responsive azobenzenes is a successful strategy to achieve a large, reversible and bi-directional (increase/decrease) switching of the thermal conductivity upon UV/Vis irradiation.

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Understanding the physics of exchange of the alkaline metal on nitrate salts mixtures with ethylammonium nitrate

Juan J. Parajó[1,2], Ana I. M. C. L. Lobo Ferreira[1], Jose M. Otero-Mato[2], Pablo Vallet[2], J. Salgado[2], Luis M. Varela[2], Luís M. N. B. F. Santos[1]*

1 CIQUP, Institute of Molecular Sciences (IMS) - Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto,
Rua do Campo Alegre, P-4169-007 Porto, Portugal
2 Grupo de Nanomateriais, Fotónica e Materia Branda, Departamento de Física de Partículas, Universidade de Santiago de Compostela,
Campus Vida s/n E-15782, Santiago de Compostela, Spain
* *lbsantos@fc.up.pt*

The technology market created the need to develop better energy storage systems. Efficiency and safety of current batteries electrolytes still present shortcomings, especially at high temperatures. Due to these disadvantages, ionic liquids (ILs) and ILs doped with salts, appear as a promising alternative to conventional electrolytes in energy fields. Although, when we are doping ILs with salts, how does this salt behaves on IL solution? Interactions among the ions in electrolyte solutions are of high interest and help in understanding the nature of the solvent. An experimental study of solution and solvation of mono- and divalent alkaline metal cations in the ethylammonium nitrate IL is reported.

The thermodynamics of solvation of alkali metal cations in a protic ionic liquid (PIL) ethylammonium nitrate (EAN) was analysed trough high precision solution-reaction calorimetry in order to obtain the heat of solvation. Enthalpy of solvation for the exchange of Li^+ for M^{v+} in EAN solution was obtained according to the scheme in Fig. 1. A close relation between the structure of the salts in the crystalline phase and its solvation enthalpy in the IL is reported. The analysis of the energetics and structure of solvation confirms the well-known water-like solvation properties of EAN. Furthermore, the results show that it is energetically more favourable to solvate smaller cations with higher valence. [1]

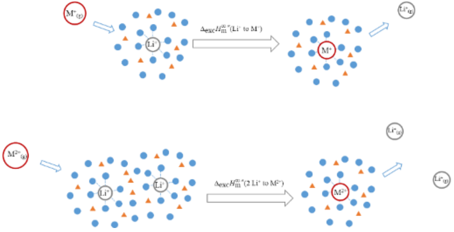

Fig.1. Exchange of M^+ (top) or M^{2+} (bottom) for Li^+ into a solution of Li^+ in EAN(l).

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Acknowledgment

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β-Amyloid aggregation or phase separation induction by electrostatic interactions with small biomolecules

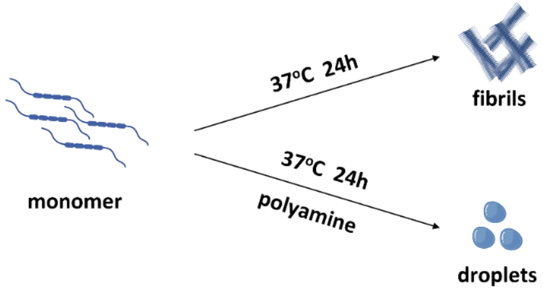
Sara Illodo[1,2,3*], **Hyeryeong Lee**[1], **Flor Rodríguez-Prieto**[2], **Mercedes Novo**[3], **Wajih Al-Soufi**[3], **Sang-Hak Lee**[1]

[1]Pusan National University, Department of Chemistry, 46241, Busan, South Korea
[2]Centro de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Departamento de Química Física, Universidade de Santiago de Compostela,15782, Santiago de Compostela, Spain
[3]Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela, 27002, Lugo, Spain
sara.illodo.brea@usc.es

β-amyloid aggregation on the brain is thought to be one the main causes of Alzheimer´s disease. β-amyloids are intrinsically disordered proteins (IDPs) that present high tendency towards aggregation into fibrils. During the aggregation process oligomeric toxic species that can induce damage to our brain are formed.[1-3]

As IDPs are prone to aggregation by molecular interactions and β-amyloids are negatively charged proteins, we thought that electrostatic interactions could be a key point on its aggregation or separation.[4] Even though metal ions, such as Cu^{2+} and Mg^{2+}, could be involved on these interactions and lead to changes in protein aggregation, small multivalent biomolecules could present a greater impact on the aggregation or phase separation.

Thus, we focused our study on the molecular mechanism underlying the protein aggregation or phase separation depending on the presence of polyamine. We carried out *in vitro* studies at different polyamines concentrations and incubation conditions using fluorescence microscopy. The preliminary results showed that there was a change in amyloid aggregation depending on polyamines. We found that the polyamine affects to protein aggregation or phase separation, observing the formation of droplets rather than fibrils.



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Nanostructured Polythiophene Materials for Electrochromism

A. Jorge Parola[1,*], Tiago Moreira[1], César A. T. Laia[1], Mattia Zangoli[2], Francesca di Maria[2]

[1]Laboratório Associado para a Química Verde (LAQV-REQUIMTE), Departamento de Química,
Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
[2]CNR-ISOF, Area Ricerca CNR, Via P. Gobetti 101, Bologna 40129, Italy
**ajp@fct.unl.pt*

Polythiophenes are semiconductor organic polymers with remarkable electrochromic properties in terms of the colour palette, colour contrast and switching times.[1] However, the implementation of electrochromic devices on industrial scale (except for PEDOT) is still hampered by stability issues in plastic or glass substrates and their processability limited to toxic organic solvents (*e.g.* chloroform). Trying to move forward in terms of processability, fast switching times and durability, we prepared novel water-dispersible nanoparticles of poly(thiophene/electron-acceptor monomers) with tunable sizes. A synthetic strategy to produce new yellow and red polythiophene materials operating at low redox potentials (Fig. 1) leading to new processable photochromic materials was developed and will be shown.[2-4] The development of a novel type of electrochromic devices using paper as substrate by assembling high-pressure laminates producing multi-layered electrochromic devices avoiding ITO or other metal oxide semiconductors will as well be presented.

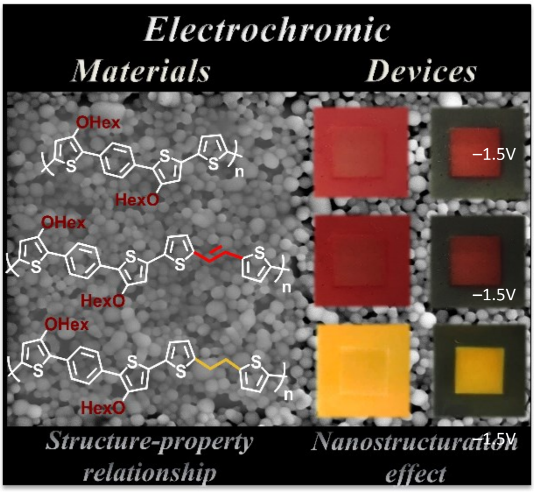

Fig.1. Structures and electrochromic devices of some of the synthesized polythiophenes.

Acknowledgements

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New insight in 4th generation battery: Pure Ionic Liquid as functional quasi-solid electrolyte

Pablo Vallet[1], Juan J. Parajó[1], Francisco J. Carretero[2], Luis M. Varela[1], J. Salgado[1]

1 Grupo de Nanomateriais, Fotónica e Materia Branda, Departamentos de Física Aplicada y Física de Partículas, Universidade de Santiago de Compostela, Campus Vida s/n E-15782, Santiago de Compostela, Spain
2 TECNALIA Research and Innovation. Donostia-San Sebastián, Euskadi, Spain
** j.salgado.carballo@usc.es*

The world energy requirements towards an energetic transition based on new forms of production and storage that allow complete sustainability and decarbonisation, involve new challenges since the clear current geopolitical instabilities. The renewable energies play and important role as a good alternative to deal with external dependency, although the intermittence in its production is the mail problem to solve. In this framework, the energy storage is playing a crucial role and the search for new and more efficient forms of energy storage is highlighted in the new European guidelines to enhance the use of the renewable energy sources.

A new battery electrolyte consisting in a pure Ionic Liquid (IL), 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, in liquid and quasi-solid forms, is presented and studied in this work. Thermal and electrochemical characterization of this compound is performed (stainless steel as blocking electrode for impedance measurements and LFP/metallic lithium as anode/catode respectively for GCPL experiences). The main advantage is that the lithium contained in the electrodes is enough to enable the charge/discharge process.

Acknowledgment
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Flavylium-cucurbit[8]uril supramolecular polymers as photorheological fluids

<u>Ambrósio Camuenho</u>[1,*], Patrícia Máximo[1], César A. T. Laia[1], Nuno Basílio[1],Rita G. Lobato[2], Maria T. Cidade[2], A. Jorge Parola[1]

[1]LAQV-REQUIMTE, FCT - Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal.
[2]i3N/CENIMAT, DCM, NOVA School of Sciences and Technology, Lisbon, Portugal.

**email: a.camuenho@campus.fct.unl.pt*

The formation of supramolecular host-guest complexes controlled by irradiation defines the field of supramolecular photorheology.[1] Flavylium cations are strongly colored dyes inspired in natural anthocyanins that can be obtained upon photoisomerization of their respective chalcones at low enough pH values.[2,3] Based on previous results [4] where it was shown that flavylium cations are able to form homoternary complexes with the cucurbit[8]uril receptor (CB8), a system was devised to develop supramolecular photorheological fluids. A 4-arm PEG macromer was derivatized with a chalcone moiety at the end of each arm, Fig 1a. Irradiation of these molecules at a suitable pH in the presence of CB8 leads to dramatic changes in the viscosity of the solution, Fig. 4b. The system reverts in the dark to the initial viscosity. Structural elucidation of the synthesized compound by 1H and FTIR-ATR, characterization of the systems by UV-Vis absorption and spectrofluorimetry to determine association constants and stoichiometries of the complex, determination of quantum yields, and the formation of hydrogel by the irradiation will be shown.

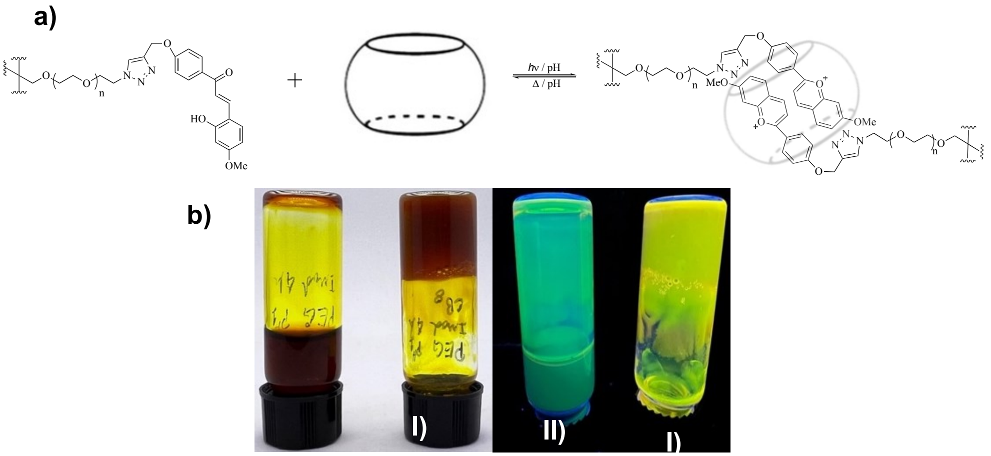

Figure 1: **a)** Formation of homoternary-based supramolecular gels between the 4-arm PEG-CT (n=55) and cucurbit[8]uril upon irradiation. **b)** 4-arm PEG-CT at pH=1: **I)** without CB[8], **II)** with CB[8] (1:2, 4% w/w). Picture were taken under white light (left) and under 365 nm light (right).

Acknowledgments

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Alkylsilane and alkylsiloxane effect on the thermodynamics of ionic liquids

Rodrigo M. A. Silva[1, *], **Hádrian Montes-Campos**[1], **Ana I. M. C. Lobo Ferreira**[1], **Eduards Bakis**[2], **Luís M. N. B. F. Santos**[1]

[1] CIQUP, Institute of Molecular Sciences (IMS) – Department of Chemistry and Biochemistry,
Faculty of Sciences, University of Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
[2] Faculty of Chemistry, University of Latvia, Jelgavas 1, Riga, LV-1004, Latvia
** rodrigo.m.a.silva98@gmail.com*

The replacement of the alkyl side chain of the cation in an ionic liquid (IL) with an alkylsilane or an alkylsiloxane chain has been shown to be a suitable way to reduce the IL's viscosity and density [1-3]. In this work we present the thermophysical study of ILs with alkylsilane and alkylsiloxane chains, as well as some carbon-based analogs, with the aim of understanding the impact of the alkylsilane and alkylsiloxane chains on their thermophysical properties. The structures of the ILs' cations are presented in Fig. 1.

The phase behavior of these compounds was studied by differential scanning calorimetry (DSC) and their heat capacity was measured, as a function of temperature (between 283 K and 333 K) by means of high-precision differential scanning microcalorimetry (*iSenseDSC*) and, at T = 298.15 K, with high-precision drop calorimetry [4]. Their thermal stability was studied by thermogravimetric analysis (TGA), and their volatility was studied by means of Knudsen effusion method coupled with a quartz crystal microbalance (KNQ) [5].

DSC experiments revealed that the IL with an alkylsiloxane group has lower melting temperature than its alkylsilane analog, and no first-order transitions were detected for the ILs with carbon-based chains. Replacing carbon with silicon also causes an increase in the molar heat capacity and in thermal stability. The vaporization study shows that the ILs with alkylsilane chains are slightly more volatile and have identical cohesive energy than their carbon-based chain analogs.

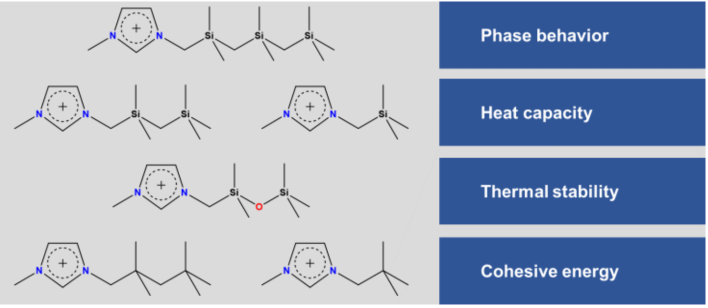

Fig.1. Cation structures and investigated properties.

Acknowlegdements

This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

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Electrical Conductivity of Ionic liquids by Multi-frequency Impedance Methodolgy

Carlos F. P. Miranda[*], **L. M. N. B. F. Santos**

CIQUP, Institute of Molecular Sciences (IMS)- Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua Campo Alegre, 4169-007 Porto, Portugal

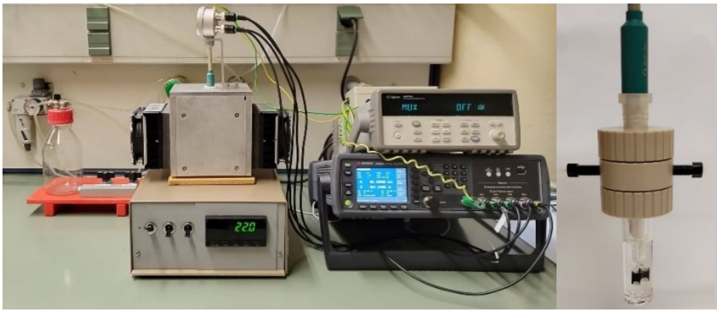
**e-mail: carlospesqueiramiranda@gmail.com*

Electrical conductivity measurements at a fixed frequency are intrinsically affected by polarization effects. Although high frequencies dimmish the impact of the polarization effect, it raises other problems associated with parasitic effects. Therefore, measuring impedance across a wide range of frequencies is the state-of-the-art procedure [1].

This work presents the development of a new system for the high precision measurement of electrical conductivity of ionic fluids. The measuring system is based on a Precision LCR meter (20 Hz - 500 kHz) from Keysight (model E4980AL) and a customized Metrohm electrical conductivity cell (model MTO-6.0908.110) installed in small sample glass vessel (8 mL) as presented in Figure 1. A customized holder of the conductivity cell was designed to insure the vacuum, gas-tight and chemical inertia of the sample container. The system is equipped with vacuum/N_2(g) lines which allows the degassing and atmospheric isolation of the sample. The temperature control is ensured by a customized air bath thermal chamber based on Peltier heat and cooling. A dedicated software application was developed to control the experimental setup as well as for data acquisition and analysis.

The results are evaluated in terms of resistance, reactance, impedance, and phase angle as functions of frequency. The correction for the polarization effect is performed using several extrapolation procedures. The extrapolation is carried by selecting the appropriate frequency range which corresponds to a region of resistance-frequency linearity.

The cell constant was experimentally determined by measuring standard aqueous 0.1 and 0.01 molal KCl solutions at different temperatures. The effects of the electrical potential level, N_2(g) flow and cell immersion depth on the temperature and signal stability were evaluated for KCl solutions and ionic liquids. The accuracy of the apparatus was evaluated by measuring a series of reference ILs.



LCR Precision Meter
Keysight E4980AL
20 Hz – 500 kHz | 4-digit resolution

Dip-in Conductivity Cell
Metrohm 6.0908.110
C_{cell} = 0.865 cm^{-1} (KCl solution)

Cell Design
Degassing & atmosphere control
Cell fixation

Temperature Stability
Peltier-based control

Customized Software
Data Acquisition & Analysis
Resistance extrapolation

Fig.1. Measuring system and conductivity cell.

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This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) through the FCT/MCTES (PIDDAC) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). Carlos F. P. Miranda is grateful to FCT for his research grant (Reference: 2020.05717.BD).

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Towards fine-tuning charge in vesicular drug delivery systems: role of spacer in cationic *gemini* surfactants at the air/water interface

Emílio V. Lage[1,*], Andrea Insua Ramos[1], Vicente Domínguez Arca[2], Gerardo Prieto[2,3], Matilde Casas[1,3]

[1]Laboratorio de Biomembranas, Departamento de Química Física, Facultade de Farmacia, Universidade de Santiago de Compostela, 15782 Santiago de Compostela,Galicia, Spain
[2]Grupo de Biofísica e Interfaces, Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago de Compostela, 15782 Santiago de Compostela,Galicia, Spain
[3]Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela,Galicia, Spain
**ev.lage.gal@gmail.com*

One of the most challenging aspects of drug delivery is how to effectively carry the drug to the desired site of action (drug targeting), and how to improve drug bioavailability. A common approach to this problem is the use of colloids as drug delivery systems, and among them, vesicles such as liposomes or niosomes [1]. As a targeting strategy, one can take advantage of the different physicochemical conditions of the microenvironment of the targeted area. Such is the presence of charged species, often in the surface of cells, which gives rise to the use of charged vesicles as drug carriers.

In order to enhance targeting and retention of the colloid in negatively charged biological environments, we propose the use of cationic *gemini* surfactants. This kind of dimeric surfactant features two classical polar head/hydrophobic chain structures, joined together by their headgroups via an alkyl spacer of variable length. It is our hypothesis that different spacer lengths will yield different molecular and thermodynamic behaviour, which will affect the arrangement of surfactant molecules and, consequently, the influence of this disposition on the surface charge of the vesicle.

As a first approach to this characterisation, we studied two *gemini* surfactant species, each made of two monomers of tetradecylammonium bromide linked by an N-alkyl-N chain of either four (14-4-14, abbreviated as GS4) or twenty (14-20-14 or GS20) methylene groups. To do so, we spread them from a chloroform solution into the air/water interface in a Langmuir trough, allowing them to spontaneously form a monolayer. We then compressed said monolayer, obtaining a compression isotherm from that process, which plots surface pressure, π (difference of surface tension of, in this case, water due to the presence of surfactants at the interface) vs mean area occupied by each molecule, A [2].

The resulting graphs for π-A isotherms of both GS4 and GS20 at 20ºC show evident differences, with GS20 experimenting a conformational change upon compression – shown as a plateau in the isotherm, which is absent in the GS4 curve. This is also proven as a dramatic drop in its compressibility modulus (C_s^{-1}). Furthermore, compression-decompression hysteresis cycles prove this conformational change irreversible. We also studied the influence of temperature and ionic strength on GS20, in an attempt to work in biomimetic conditions. The energy distribution changes with temperature as expected, increasing the population of molecules which can overcome the energy barrier for the conformational change. The addition of NaCl seems to counter this effect, probably because of dehydration mediated by a salting-out effect.

These results prove these gemini surfactants, particularly GS20, are interesting and their interaction with other surfactants that make vesicles, such as lipids and non-ionic surfactants, is worth studying, and this behaviour may prove essential for charge distribution at the vesicle surface.

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Environmental mobility of pesticides and agrochemical metabolites: volatility and phase transitions properties of some dichlorobenzonitrile isomers

Bruno D. A Pinheiro*, **Ana R. R. P. Almeida, Manuel J. S. Monte**

Research Center in Chemistry of University of Porto (CIQUP), Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry (DQB), Faculty of Sciences of University of Porto (FCUP), Porto 4169-007, Portugal
**up201100352@edu.fc.up.pt*

The environmental fate of pollutants can be evaluated through the experimental determination and subsequent prediction of important physical-chemical properties of those substances. Some of these parameters can be determined from a thermodynamic study on the volatility and phase transitions equlibria of crystalline or liquid compounds [1]. The present work reports experimental vapor pressures at different temperatures of five dichlorinated isomers of benzonitrile – a well-known family of organic chemical pollutants. The sublimation vapor pressures of 2,3-, 2,6-, 3,4- and 3,5- dichlorobenzonitriles were determined using the Knudsen mass-loss effusion method [2]. Besides, the vapor pressures of the crystalline phase of 2,6-dichlorobenzonitrile (dichlobenil) and of both condensed phases (crystalline and liquid) of the 2,4- isomer were measured by a diaphragm manometer static method [3]. From the experimental results, the standard molar enthalpies, entropies and Gibbs energies of sublimation of the five compounds and of vaporization of 2,4-dichlorobenzonitrile were derived. The phase diagram representation of the (*p*,*T*) results of the latter substance, in the neighborhood of the triple point, was plotted. The thermal analysis of these compounds was also performed using differential scanning calorimetry, enabling the determination of their temperatures and molar enthalpies of fusion as well as the respective isobaric crystalline heat capacities at different temperatures.

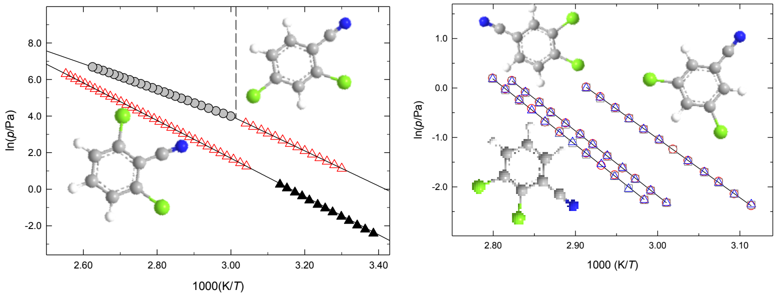

Figure 1: Plots of ln*p* against 1/*T* for the five dichlorobenzonitriles studied.

Acknowledgments
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QUÍMICA INORGÁNICA

Dinuclear copper(II) complexes as models for metalloenzymes

I. Velo-Heleno[1,*], **S. Fernández-Fariña**[1], **L. Rouco**[2], **U. Barreiro**[1], **A. M. González-Noya**[1]

[1]Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Campus Vida, 15782, Santiago de Compostela, Spain
[2]Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Terra, 27002, Lugo, Spain
e-mail: mariaisabel.velo.heleno@usc.es

Recently, the design and synthesis of metallo-supramolecular architectures that mimic the active sites of metalloenzymes have caused great interest due to these artificial models can contribute to understanding the function and mechanism of action of these enzymes. For this reason, the study of these biomimetic models could allow the development of systems with properties similar to those of natural metalloenzymes.[1,2]

An extensive variety of metal ion-derived enzymes are found in nature, capable of catalysing a wide range of reactions under mild conditions and with high selectivity.[3] In this work, we will approach the synthesis and characterization of dinuclear copper(II) complexes as possible models of natural redox metalloenzymes such as catalase, superoxide dismutase and peroxidase.

For this purpose, we have designed a family of pentadentate [N_2S_2O] bisthiosemicarbazone ligands H_3L^n (n=1, R=Me; n=2, R=Et; n=3, R=Ph) capable of stabilising copper(II) complexes. Dinuclear neutral copper(II) compounds [$Cu_2L^n(OH)$] (Figure 1) have been prepared by using an electrochemical methodology. These complexes have been fully characterized in solid state and in solution, showing that are assembled into tetranuclear clusters [$Cu_2L^n(OH)]_2$.

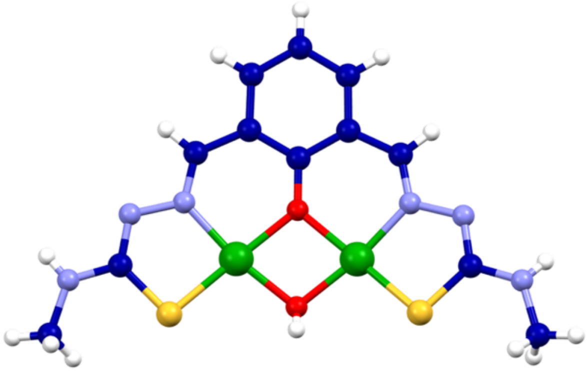

Fig.1. Dinuclear copper(II) complex [$Cu_2L^1(OH)$].

Acknowledgments

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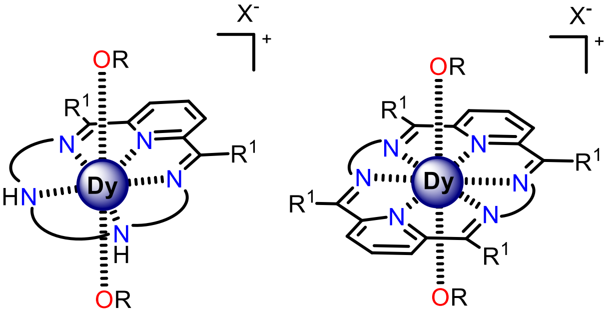
Single ion magnets of macrocyclic N_5 and N_6 ligands

Cristina González-Barreira[1,*], **Julio Corredoira-Vázquez**[1,2], **Paula Oreiro-Martínez**[1], **Matilde Fondo**[1]

[1] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2] Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal
**cristina.gonzalez.barreira@rai.usc.es*

The broad interest on the field of single molecule magnets (SMMs) is mainly ignited by the potential applications of SMMs in storage and processing of digital information, as well as in quantum computing.[1] But one of the great challenges in this field is still to obtain molecule magnets with high blocking temperatures that are stable in air. In the search for such molecular materials, one area of growing interest is that of single ion magnets of Dy^{III} with strongly axial pentagonal or hexagonal bipyramidal geometry (pbp or hbp), making use of equatorial plane-delimiting N_5 or N_6 donor macrocyclic ligands and bulky anionic monodentate oxygen donors in the apical positions.[2] This field is still in its infancy, but synthetic strategies to obtain pure compounds and to increase the energy barrier for spin reversal are emerging. Recent advances in this particular topic are presented in this communication.



(≡ alipatic chain, aliphatic or aromatic ring

OR = alkoxide or aryloxide group
R^1 = donor or electron withdrawing group
X = bulky anion

Fig.1. Schematic representation of Dy^{III} complexes with macrocyclic N_5 or N_6 donors and pbp or hbp geometry.

Acknowledgments
Authors thank the Spanish Ministerio de Innovación, Ciencia y Universidades (PGC2018 102052-B-C21), and Xunta de Galicia for financial support. J.C.V. also thanks Xunta de Galicia for his postdoctoral fellowship (ED481B-2022-068).

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Direct C-H arylation of dithiophene-tetrathiafulvalene: tunable electronic structure and 2D self-assembled molecular networks on surface

Catarina Ribeiro[1], Gonçalo Valente[1], Rafaela A. L. Silva[2], Dulce Belo[2], and Manuel Souto[1]

[1]Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Portugal
[2]Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10, P-2695-066 Bobadela LRS, Portugal
**catarina.gribeiro@ua.pt*

Tetrathiafulvalene (TTF) and its derivatives represent a class of electron-donor molecules widely explored in the field of molecular electronics, leading to a plethora of organic conducting materials with exotic physical properties [1]. Arylated TTF has been also used in extended structures, such as macrocycles, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) [2]. Among its derivatives, dithiophene-tetrathiafulvalene (DT-TTF) received considerable attention as active material for organic field-effect transistors (OFETs) due to its high charge carrier mobility [3,4]. However, so far, no studies on the direct functionalization of DT-TTF building blocks in order to modulate its electronic structure have been reported. Herein, we report the direct C-H arylation of DT-TTF (**1**) to synthesize mono- (**2**, **3**) and tetraarylated (**4**, **5**) derivatives bearing different electron-donor or electron-withdrawing groups in order to modulate its electronic structure (Fig. 1). In addition, the formation of 2D self-assembled networks of DT-TTF-tetrabenzoic acid (H_4DT-TTFTB, **5**) was visualised by scanning tunneling microscopy.

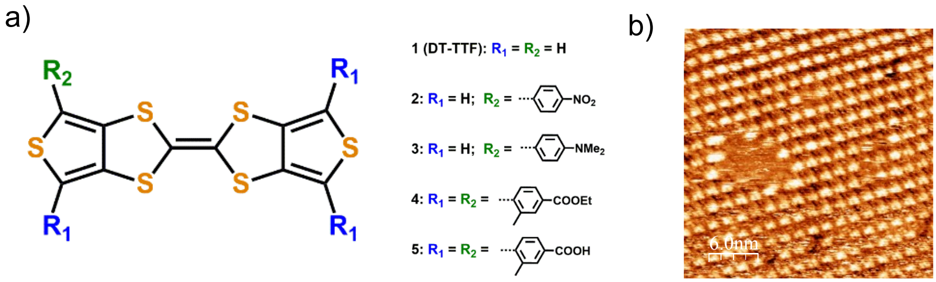

Fig.1. a) Molecular structures of arylated DT-TTF derivatives and b) STM image of physisorbed layer of **5** on HOPG.

Acknowledgements

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Atmospheric carbon dioxide activation by a cobalt complex

Laura Rodríguez-Silva[1,*], **Lara Rouco**[1], **M. Isabel Fernández-García**[1],
M. Isabel Velo-Heleno[2], **Marcelino Maneiro**[1]

[1]Universidade de Santiago de Compostela, Facultade de Ciencias, Campus Terra, 27002 Lugo, Spain.
[2]Universidade de Santiago de Compostela, Facultade de Química, Avda. das Ciencias s/n, 15701
Santiago de Compostela, Spain
**laura.rodriguez@usc.es*

Carbon dioxide is one of chemicals that more contributes to the greenhouse effect. An attractive approach is carbon dioxide valorisation, The CO_2 can be captured and subsequently converted into various valuable chemicals. Among the different approaches for CO_2 atmospheric fixation, metal complexes arise as one of most inexpensive and attractive way to capture this waste product. Herein, we report a new type of complexes of inexpensive first-row metals, using bis(amine)-bis(phenolate) ligands (H_2L), that can fix atmospheric carbon dioxide.

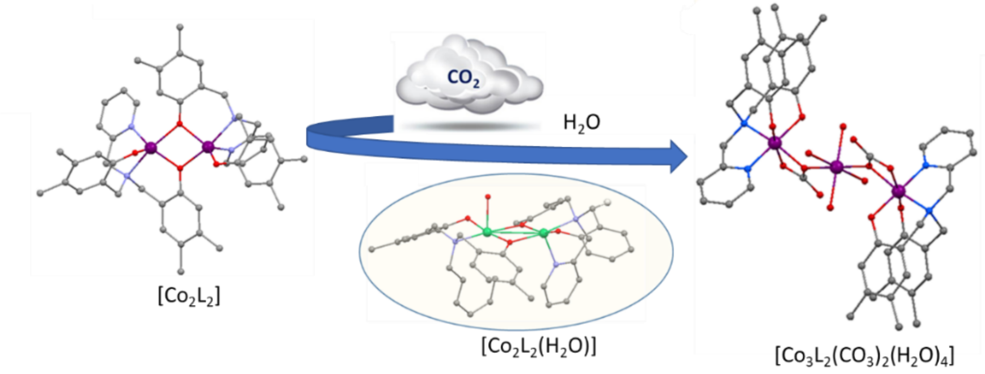

Fig.1. Proposed mechanism for the formation of carbonate derivative

A dinuclear cobalt complex $[Co_2L_2]$ incorporating a bis(amine)-bis(phenolate) ligands was obtained by electrochemical oxidation in non-aqueous conditions. [1,2] The cobalt dimer complex $[Co_2L_2]$ reacts with CO_2 to form a bridging carbonate complex (μ-η^1,η^2-CO_3). The $[Co_2L_2]$ complex appears as an efficient and selective model for atmospheric CO_2 capture and subsequently conversion to carbonate. A possible mechanism to explain the formation of the carbonate derivative, should involve the initial formation of the intermediate $[Co_2L_2(H_2O)]$, which reacts with CO_2 and leads to the formation of the carbonate complex (Figure 1). Progress on the obtention of chemical value derivatives from these CO_2 fixation processes will be also discussed.

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An efficient route to coinage metal mesocates

S. Fernández-Fariña[1,*], **I. Velo-Heleno**[1], **L. Rouco**[2], **L. Rodíguez-Silva**[2], **R. Pedrido**[1]

[1]Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Terra, 27002, Lugo, Spain
**sandra.fernandez.farina@usc.es*

Mesocates have been presented in the literature as a type of metallosupramolecular structure [1]. However, mesocates have been much less studied than helicates despite of they also exhibit high potential in fields like nanomaterials [2] and nanomedicine [3,4].

In this communication we report a simple and efficient route for the selective synthesis of metal(I) mesocates, combining a suitable designed thiocarbohydrazone ligand and an electrochemical procedure (Figure 1). Our findings are strongly supported by different characterization techniques such as X-ray diffraction studies, IR and the MS MALDI and ESI studies. Thus, our double strategy based on the ligand design and the synthetic procedure provides a feasible electrochemical pathway to coinage dinuclear mesocates [5].

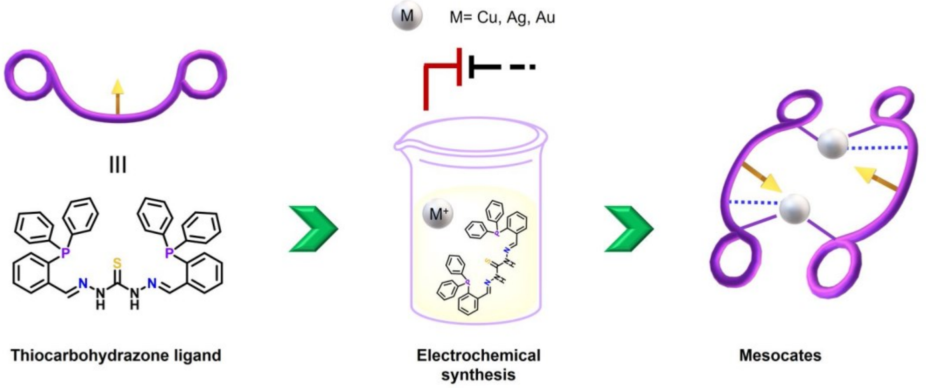

Fig.1. A selective pathway towards coinage metal mesocates.

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A dysprosium field-induced single molecule magnet with a N_3O_2 flat donor

Julio Corredoira-Vázquez[1,2*], **Paula Oreiro-Martinez**[2], **Ana M. García-Deibe**[2], **Jesús Sanmartín-Matalobos**[2,3], **Matilde Fondo**[2]

[1]Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal
[2]Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[3] Institute of Materials (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
**julio.corredoira.vazquez@usc.es*

In recent years, the search for new molecular-based materials has been a very active area of research, and the field of molecular magnets occupies a preferential position within it. These magnets exhibit characteristics that are not possible to observe in the classical ones, such as bifunctionality. Within the molecular-based magnets, single molecular magnets (SMMs) are a group of increasing relevance [1].

The functionality of SMMs depends on its structure, and the control of the coordination geometry around the lanthanoid ion is a key factor for manipulating the magnetic properties of the system. Many synthetic strategies have been designed to improve the blocking temperature (T_B) and effective energy barrier for the spin reversal (U_{eff}) in SMMs, and one of them is to obtain dysprosium complexes with and axial symmetry, such as pentagonal bipyramid [1],[2].

In light of the above considerations, we describe herein the synthesis and full structural and magnetic characterization of the dysprosium complex $[Dy(L)(Cl)(H_2O)_2]$ (**1**) (Figure 1, left) from the pentadentate Schiff base ligand H_2L. Magnetic *ac* studies show that the compound exhibits SMM behaviour induced by an external magnetic field (H_{dc}) (Figure 1, right).

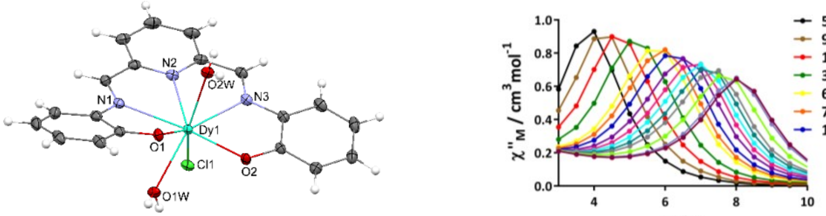

Fig.1. Ellipsoids diagram (50% probability) for **1** (left), and temperature dependence of c’’$_M$ for **1** in a *dc* applied field of 1500 Oe at different frequencies (right)

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QI07

Síntese, caracterización e estudo das propiedades biolóxicas de *E,Z*-[RuCl(η^6-*p*-cimeno)(κ^2*N*3,*S*-TSC)]$^+$ (TSC = tiosemicarbazona)

M. Martínez-Estévez[1,*], **S. García-Fontán**[1], **S. Argibay**[1], **I.Prieto**[2], **E.M. Vázquez-López**[1]

[1] *Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur, Facultade de Química, Universidade de Vigo, E-36310 Vigo, Galicia, España.*
[2] *Departamento de Química-Física, Facultade de Química, Universidade de Vigo, E-36310 Vigo, Galicia, España.*
**e-mail del autor de contacto: monmartinez@alumnos.uvigo.es*

O estudo de novos axentes antitumorais incrementouse nas últimas décadas como alternativa ó *cis*-[$PtCl_2(NH_3)_2$] e ós seus análogos. En concreto, destacan os complexos de rutenio mostrando unha maior actividade fronte a cancros primarios e tumores metastáticos. [1,2]

Nesta comunicación descríbese a síntese, caracterización estrutural e estudo da actividade antitumoral *in vitro* fronte a liñas celulares de carcinoma de pulmón (NCl-G460), de adenocarcinoma humano (A549) e de cancro de mama triplo negativo (MDA-MB231) do ligando tiosemicarbazona (TSC) así como do correspondente catión complexo [RuCl(k^{6}C^1-*p*-cimeno)(k^{2}N3,S- TSC)]$^+$.

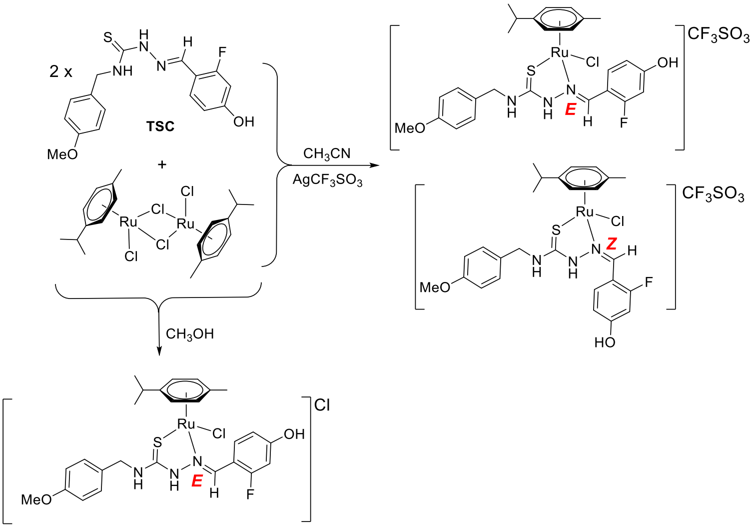

Figura 1: Esquema da síntese dos complexos con fórmula xeral [RuCl(κ^6C^1-*p*-cimeno)(κ^2N3,S-TSC)]$^+$

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QI08

Au(III) π-Allyl Complexes: From Structure Analysis to Catalysis

Jessica Rodriguez[1],*, Didier Bourissou[1]

[1] Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier/CNRS UMR 5069, 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France)
** jessicarodriguez.villar@usc.es*

π-Allyl complexes play a prominent role in organometallic chemistry, in particular within the frame of the Pd-catalysed Tsuji–Trost reaction. This prompted us to explore Au(III) π-allyl complexes, which had remained so far elusive species.[1] The π coordination of allyl moieties to (P,C) cyclometallated Au(III) complexes was authenticated. The resulting (P,C)Au^{III}(π-allyl) complexes were readily isolated as thermally and air-stable solids. Spectroscopic and crystallographic analyses combined with detailed DFT calculations support tight quasi-symmetric η^3-coordination of the allyl moiety.

The π-allyl Au(III) complexes are activated towards nucleophilic additions.[2] The reactivity of (P,C)Au^{III}(π-allyl) complexes toward β-diketo enolates was thoroughly studied. Meticulous NMR experiments combined with DFT calculations revealed a complex and rich mechanistic picture. Nucleophilic attack can occur at the central and terminal positions of the π-allyl as well as the metal itself (Fig. 1a). All paths are observed and are actually competitive, whereas addition to the terminal positions largely prevails for Pd(II). Auracyclobutanes and π-alkene Au(I) complexes were authenticated spectroscopically and crystallographically, and Au(III) σ-allyl complexes were unambiguously characterized by multinuclear NMR spectroscopy. Nucleophilic additions to the central position of the π-allyl and to gold are reversible. Over time, the auracyclobutanes and the Au(III) σ-allyl complexes evolve into the π-alkene Au(I) complexes and release the C-allylation products. The relevance of auracyclobutanes in gold-mediated cyclopropanation was demonstrated by inducing C–C coupling with iodine. The reaction profiles for the addition of β-diketo enolates were thoroughly studied by DFT.

On the other hand, the (MeDalphos)AuCl complex was found to efficiently catalyze the cross-coupling of indoles and allyl acetates/alcohols (Fig. 1b).[3] The reaction tolerates many functional groups and selectively affords the branched C3-allylated products from both a- and g-substituted allyl substrates. It takes advantage of the hemilabile character of the P^N ligand. The C(sp^2)–C(sp^3) coupling operates via a Au(I)/Au(III) redox cycle and involves a dicationic π-allyl Au(III) complex as key intermediate. In this case, the allyl moiety adopts an asymmetric σ + π-coordination mode, as substantiated by NMR spectroscopy and DFT calculations.

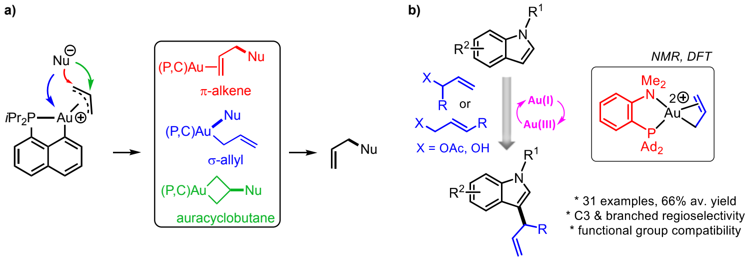

Fig.1. a) Possible reactive sites for the addition of nucleophiles to π-allyl complexes; b) (P,N)AuCl-catalyzed coupling of indoles and allyl acetates, with a π-allyl Au(III) complex as key intermediate.

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QUÍMICA ORGÁNICA

Síntesis de nuevos sesquiterpen-polifenoles, actividad citotóxica y estudios de acoplamiento molecular inducido (*Docking*)

Ileana Araque E.[1,2]*, Jaime Mella R.[2], Juan Villena[3], Javiera Ramírez [1], Mauricio Cuellar F.[1*]

[1]Centro de Investigación Farmacopea Chilena, Escuela de Química y Farmacia, Facultad de Farmacia, Universidad de Valparaíso, Av. Gran Bretaña 1093, Valparaíso, Chile.
[2]Instituto de Química y Bioquímica, Facultad de Ciencias, Universidad de Valparaíso, Av. Gran Bretaña 1111, Valparaíso, Chile.
[3]Centro de Investigaciones Biomédicas (CIB), Escuela de Medicina, Universidad de Valparaíso, Av. Hontaneda N° 2664, Valparaíso, Chile.
**e-mail del autor de contacto: ileana.araque@postgrado.uv.cl, mauricio.cuellar@uv.cl*

El árbol de canelo de Magallanes (*Drimys winteri*) constituye una de las especies vegetales más representativas de Chile. Los metabolitos drimánicos obtenidos de esta especie han despertado especial interés en los últimos años gracias a sus propiedades bioactivas como antimicrobianos, antifúngicos y su alto potencial en diversas patologías, entre las que se incluye al cáncer.[1] El estudio de la proteína 3-fosfoinositida dependiente de la proteína quinasa-1 (PDK1) como diana farmacológica para el tratamiento del cáncer es de gran interés, pues PDK1 se localiza entre las vías más comúnmente alteradas en el cáncer y su sobreexpresión se relaciona con el desarrollo de varios tipos de carcinoma.[2] En recientes estudios se ha reportado al derivado de drimano, neoalbaconol, como un inhibidor efectivo de la diana farmacológica PDK1, por lo que el estudio de este compuesto y sus análogos brinda una base sólida en la síntesis de nuevos agentes antineoplásicos de estructura drimano-orcinol.[3] En el presente trabajo se llevó a cabo la síntesis de 13 nuevos análogos de neoalbaconol de estructura aril drimánica, con un enlace puente de tipo éster, partiendo del metabolito drimenol obtenido de *Drimys winteri* (Figura 1a-b).

Se evaluó la actividad antiproliferativa de los compuestos sintetizados en las líneas celulares MCF-7, PC-3 y HT-29, utilizando MCF-10 como control y la capacidad inhibitoria de PDK1 de los mejores candidatos sintetizados a través de acoplamiento molecular inducido (*Docking*). La molécula que incluyó un fragmento orcinol presentó los mejores resultados de citotoxicidad con un IC50 de 33.7 +/- 1.3 µM, 56.9 +/- 4 µM y 67.2 +/- 7.1 µM, respectivamente. A su vez, mostró ser un buen inhibidor de PDK1, observándose 2 interacciones de puente de Hidrógeno con Lys 163 y Tyr 161. (Figura 1c). El presente estudio busca contribuir al estudio, obtención y aprovechamiento de los metabolitos secundarios extraídos desde fuentes naturales para la generación de nuevas moléculas de estructura drimánica con capacidad anticancerígena.

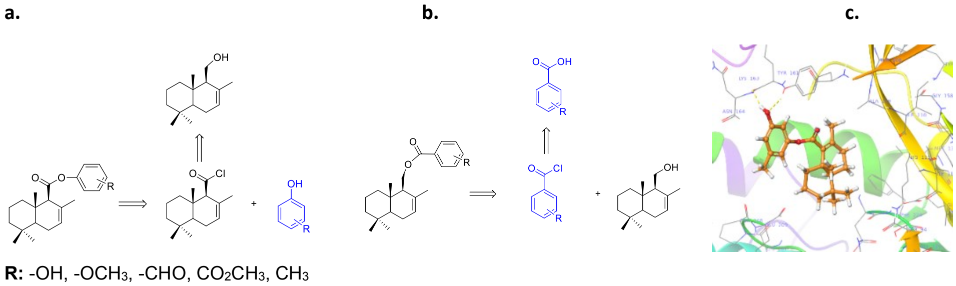

Figura 1. a. Molécula representativa del estudio; b-c: Análisis retro sintético para la obtención de nuevos derivados con estructura general de sesquiterpen-orcinol; d: *Docking* molecular representativo del estudio en PDK1 (PDB: 4RRV).

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Síntese de análogos de nucleósidos e nucleótidos baseados em unidades de D-glucuronamida e contendo um anel 1,2,3-triazole potencialmente bioativos

***Manuel, Domingos M.; Xavier, Nuno M.**

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Ed. C8, 5° Piso, Campo Grande, 1749-016 Lisboa, Portugal.
*e-mail: moraisbwill@gmail.com e nmxavier@fc.ul.pt

Os nucleósidos e nucleótidos constituem classes importante de biomoléculas que desempenham papéis essenciais em processos fisiológicos vitais como a síntese dos ácidos nucleicos, divisão celular, metabolismo ou sinalização celular. Estes eventos biológicos encontram-se desregulados em várias doenças, como o cancro ou infeções virais, o que tem motivado a procura de bibliotecas de compostos análogos ou miméticos a nucleós(t)idos de modo a interferirem/inibirem esses processos [1,2]. No entanto, algumas limitações têm sido associadas ao uso clínico destas moléculas, nomeadamente a sua baixa biodisponibilidade e o surgimento de resistência quimioterapêutica [1]. A concepção e síntese de novas estruturas bioativas análogas a nucleós(t)idos que possam ultrapassar estas limitações, potenciar mecanismos de ação alternativos e abrir novas oportunidades terapêuticas, é de interesse significativo.

Neste contexto, nesta comunicação é reportada a síntese de uma variedade de análogos/miméticos de nucleósidos, nucleótidos e difosfato de açúcares construídos em unidades de D-glucuronamida, que são unidades glicosilícas pouco exploradas em química dos nucleósidos, e que contêm um anel 1,2,3-triazole. O sistema triazole foi planeado como um substituto de uma base azotada ou como um potencial sistema mimético neutro e relativamente estável do grupo fosfato e foi combinado a outros grupos como fosfonato ou amida de modo a estabelecer um potencial fragmento mimético de um sistema difosfato. As metodologias sintéticas utilizaram azido piranoses e D-glucofuranuronolactona como precursores e empregam etapas-chave tais como a cicloadição azida-alcino 1,3-dipolar, *N*-glicosilação, ou a reacção de Arbuzov. Estudos posteriores de avaliação da atividade biológica revelaram a atividade significativa de algumas das moléculas sintetizadas contra linhas de células cancerígenas, demonstrando o interesse terapêutico de nucleósidos baseados em D-glucuronamida.

Agradecimentos:
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QO03

Nitrones' rearrangements: 7 WONDERS

Ricardo A. L. S. Santos[1,*], Artur M. S. Silva[1], Diana C. G. A. Pinto[1]

[1] LAQV-REQUIMTE & Chemistry Department, University of Aveiro, Portugal
**ricardossantos@ua.pt*

The nitrones (imine *N*-oxides) are a family of compounds whose name was given by Pfeiffer in 1916 [1]. Their structure is composed of a central cationic nitrogen, single-bonded to an anionic oxygen and to one carbon, and double-bonded to another carbon, which provides an interesting reactivity. It is easy to prepare, and it can be converted to heterocycles and nitrogenated products. The available routes are unaccountable. Only in rearrangements, there are seven selective transformations (7 WONDERS), depending on the conditions: Behrend rearrangement; electrocyclization; presence of *N*-vinyl or adjacent leaving groups; isomerization to oximes and oxazolines; cyclization to oxaziridine; Beckmann rearrangement; rearrangement of *α,β*-unsaturated nitrones. They are related to the nitrones' stability [2,3,4,5,6,7,8].

These reactions compose one section of a short, comprehensive and actualized nitrones' review, to be published soon by the authors. They are carefully organized to simplify their understanding, by bond's liability and the distance and direction of athoms' migration. Their mechanisms are explained as well. Hence, knowledge can be easily used as a tool in scientific discovery.

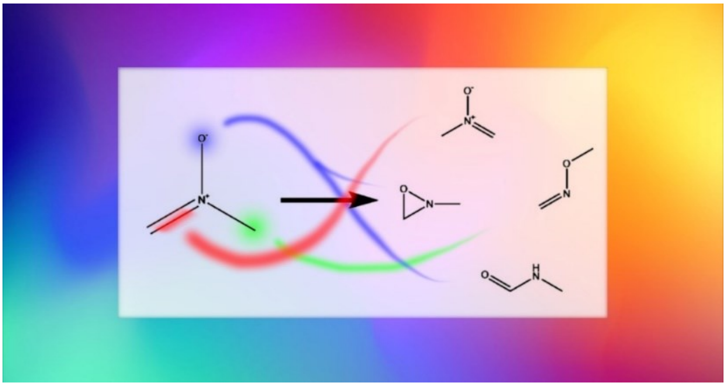

Fig.1. Graphical Abstract – three rearrangement types of nitrones (subdivided in the 7 reactions).

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Multistate of chemical reactions of 7-diethylamino-4´-dimethylaminoflavylium. Thermodynamics, kinetics and Photochemistry modulated by water: ethanol, SDS and CTAB micelles

P. Araújo[1]*, N. Basílio[2], A. Jorge Parola[2], V. de Freitas[1], J. Oliveira[1], F. Pina[2]

[1] Laboratório Associado para a Química Verde – REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal,
[2] Laboratório Associado para a Química Verde – REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal,
** up200700800@fc.up.pt*

Aminoflavylium compounds are an interesting family of compounds exhibiting physical chemical properties suitable for different applications beyond those of anthocyanins in food and health [1,2].

In general, all species of the aminoflavylium multistate of species are stable in all pH range, including basic medium, exhibit a rich color pallet, making them appropriate to design sensors or new photochromic systems, for example. However, most aminoflavylium compounds have a severe drawback, because are scarcely soluble in water. In this sense, different micellar systems have been studied to improve the solubility of these pigments.

The photochromic properties of the *mono* and *bis* aminoflavylium base systems, have been extensively studied in organic solvents, polymers and water: ethanol (1:1), by Matshushima and co-workers [3,4]. In particular the photochromic systems based in *bis*-aminoflavylium have a blue output upon irradiation of the yellow *trans*-chalcone [5].

In this work the thermodynamics and kinetics of the compound 7-diethylamino-4'-dimethylaminoflavylium was studied in water:ethanol (1:1) in the presence of SDS and CTAB micelles. The blue flavylium cation is in equilibrium with the pink protonated flavylium cation defined by $pK_{AH2+/AH+}$ and the yellow *trans*-chalcone, defined by $pK_{AH+/Ct}$. The difference between these two p*K*s gives the pH domain of the flavylium cation, $\Delta pK=1.95$ in CTAB, $\Delta pK=5.6$ in water:ethanol (1:1) and $\Delta pK=8.5$ in SDS micelles. On the other hand, the pH domain of the *trans*-chalcone is limited by $pK_{AH+/Ct}$ and $pK_{Ct/Ct-}$. It is lower in SDS micelles $\Delta pK=2.7$, increases in ethanol:water (1:1) $\Delta pK=5.1$ and is maximum in CTAB micelles, $\Delta pK=6.8$. All these effects can be explained by the electric charge of the micelles surface.

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Synthesis and anti-*Candida* Activity of Aminated Thioxanthones

Joana C.[1,2,3,*], **Joana F.S.**[2,3], **Fernando D.**[1,3], **Madalena P.**[1,3], **Emília S.** [1,3,*], **and Eugénia P.**[2,3]

[1]Laboratory de Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2]Laboratory of Microbiology, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[3]Interdisciplinary Centre of Marine and Environmental Research (CIIMAR), University of Porto, 4450-208 Matosinhos, Portugal
*joanina_cardoso@hotmail.com; esousa@ff.up.pt

Candida infections are a major cause of mortality and morbidity with *C. albicans* being the most frequently associated pathogenic fungi. The increasing worldwide incidence and severity of these fungal diseases are mainly due to the intrinsic or acquired resistance of *Candida* species to the few commercial antifungals available, resulting from excessive and/or inappropriate use. [1,2] Considering that thioxanthones are bioisosteres of xanthones with known anti-infective actions, the discovery of new antifungals with a thioxanthone scaffold could be considered a promising approach to renew the therapeutic arsenal, and control the emergence of infections by new fungal agents and the development of resistances. [3,4] Thus, the present work involves the synthesis of thioxanthone derivatives and, subsequently, the evaluation of their activity against a diversity of *C. albicans* strains with different susceptibility profiles to azoles.

The aminated thioxanthones were synthesized by Ullmann cross-coupling reactions from a chlorinated thioxanthone and a primary amine. Their effect against *C. albicans* was evaluated using the broth microdilution method by minimum inhibitory concentration determination. Among the tested compounds, one thioxanthone showed promising antifungal activity, especially against fluconazole-resistant strains of *C. albicans* and, therefore, studies of anti-virulence activity were performed. The newly synthesized compound appears to inhibit two important virulence factors - dimorphic transition and biofilm formation - frequently associated with *C. albicans'* pathogenicity and resistance. These findings suggest the possibility of aminated thioxanthones as a new alternative to the conventional treatment of *Candida* infections, including by fluconazole-resistant strains.

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Chiral pool synthesis of new flavones with potential antitumor activity

Cláudia Pinto[1*], Flávia Barbosa[2], Daniela Pereira[1,3], Odília Queirós[2], Madalena Pinto[1,3], Honorina Cidade[1,3], Maria Elizabeth Tiritan[1,2,4*]

[1] Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal
[2]Oral Pathology and Rehabilitation Research Unit, University Institute of Health Sciences (IUCS), CESPU, Portugal
[3]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal
[4]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, CESPU, CRL, Portugal
*elsaferreira1971@hotmail.com; beth@ff.upt

Cancer remains as the major public health problem worldwide, whose incidence continues to increase despite the multiple efforts in both diagnosis and prevention [1].

Flavonoids are an important class of pharmacological active compounds with multiple structures widely present in fruits and vegetables [2]. Many of them are chiral and have been identified in epidemiological studies as potential antitumor agents through the interference with several molecular targets beyond mitigating the occurrence of side effects and multidrug resistance problems [3]. Moreover, given the importance to evaluate both enantiomers in biological activities, some synthetic chiral flavonoids have been developed by different approaches as promising antitumor agents [4, 5].

This work reports the synthesis of a small library of chiral derivatives of flavonoids (CDF) through stereoselective synthesis of four different flavones scaffolds following the chiral pool approach. The success of enantioselective synthesis was proven by liquid chromatography with enantiomeric ratio values above 89%. The evaluation of their antiproliferative activity on three human tumor cell lines demonstrated that chiral derivatives have better activity compared to the precursors, being derivative TriCe-DTrp with a tryptophan moiety the most potent. Interestingly, enantioselectivity was also demonstrated, namely on TriCe-LTyr/TriCe-DTyr pair, where the L-enantiomer has practically no activity compared to its enantiomer. The evaluation of the mechanisms underlying the activity of the most promising compounds is ongoing.

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Influence of proton transfer on the luminescence of organic dyes

<u>Samuel Guieu</u>[1,2,*], Luís F. B. Fontes[1,2], Cátia I. C. Esteves[1], Ana F. N. Borges[1], Raquel Nunes da Silva[1], Sara Gil-Guerrero[2], Manuel Melle-Franco[2], João Rocha[2], Artur M. S. Silva[1]

[1]LAQV-REQUI*M*TE and Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal
[2] CICECO-Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal
**sguieu@ua.pt*

The dynamic nature of proton transfer and its effect on the photophysical properties of organic dyes is an attractive strategy to create responsive probes and materials. If the dyes have an intramolecular hydrogen bond offering the possibility of tautomerism, their photophysical behaviour may become more difficult to rationalize, and this may impede their applications.

Different series of intramolecularly hydrogen-bonded organic dyes have been synthesized and characterized (Fig.1). Their structures have been varied using different backbones (chalcone, pyridine, phenol) decorated with donor and acceptor substituents, to perceive the influence of each substitution on their photophysical properties. The susceptibility of these moieties to pH variations has also been studied, elucidating that the level of protonation had a significant effect on the emission intensity and colour. The assignment of each emission band was made using DFT and td-DFT calculations, that were in agreement with the experimental results, allowing the rationalization of the emissive processes.

This study emphasizes the versatility of organic dyes, which can be synthetized and tuned effortlessly, in order to have the desired proton transfer modulation and subsequent emission response.

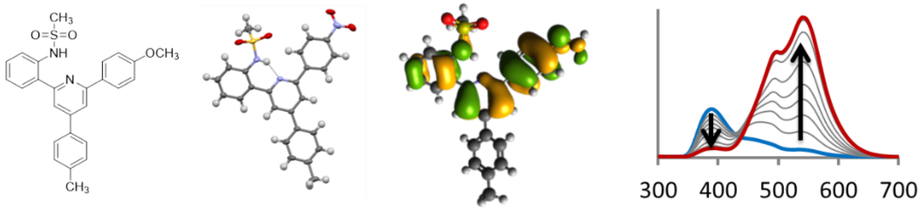

Fig.1. Illustration of the chemical structure, crystal structure, molecular orbitals and emission spectra of the dyes

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Estrategia sintética para la obtención del primer análogo tipo Gemini del maxacalcitol

<u>Sánchez-Sanz I.</u>[1,*], **Santalla H.[1]**, **Fall Y.[1]**, **Gómez G.[1]**

[1]Departamento de Química Orgánica, Facultad de Química, Universidade de Vigo, Campus
Universitario Lagoas-Marcosende, Vigo, España.
**irenesanchezsanz24@gmail.com*

En las últimas décadas se han estudiado los análogos de la 1α,25-dihidroxivitamina-D_3 o calcitriol, la forma activa de la vitamina D_3, como potenciales fármacos frente a numerosas enfermedades debido a su mayor selectividad por las funciones no clásicas de esta hormona, entre las que se incluyen el control del sistema inmunitario, la actividad antiproliferativa y la inducción a la apoptosis en las células tumorales.[1]

Se ha comprobado que análogos con un átomo de oxígeno en posición 22 presentan una elevada eficacia en el tratamiento de enfermedades autoinmunes,[2] como ejemplifica el uso del maxacalcitol para inhibir la proliferación de queratinocitos, causante de la psoriasis, o la utilización del lexacalcitol para prevenir el rechazo durante el trasplante de órganos.[3]

Por otro lado, los análogos con una doble cadena lateral, conocidos como análogos tipo Gemini, han demostrado una elevada selectividad por la actividad antiproliferativa y grandes resultados en la reducción del volumen tumoral en numerosos tipos de cáncer.[4]

En este contexto, hemos llevado a cabo la síntesis del primer análogo tipo Gemini del maxacacalcitol, aunando las caractertísticas estructurales de ambos tipos de análogos, para su posterior evaluación biológica como potencial citostático frente a diferentes líneas celulares. Para ello, se ha desarrollado una nueva metodología que permite el control total sobre la estereoquímica del carbono 20 y que se caracteriza por una gran versatilidad, pudiendo ser utilizada para la síntesis de análogos similares tipo Gemini con un átomo de oxígeno en posición 22.

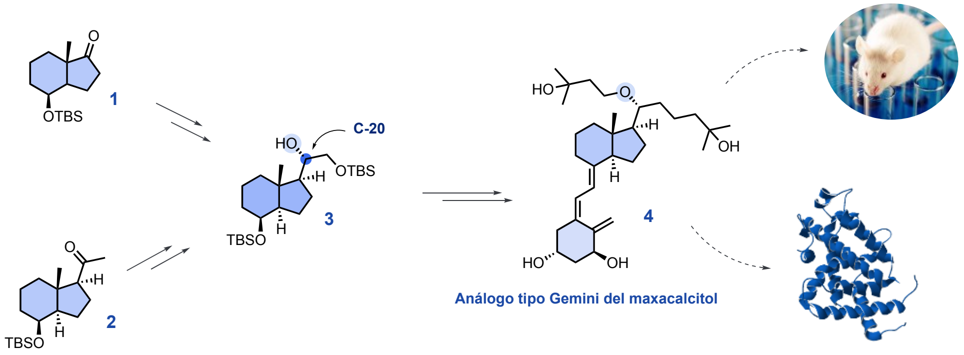

Fig. 1. Resumen de las rutas sintéticas que permiten obtener el análogo tipo Gemini del maxacalcitol.

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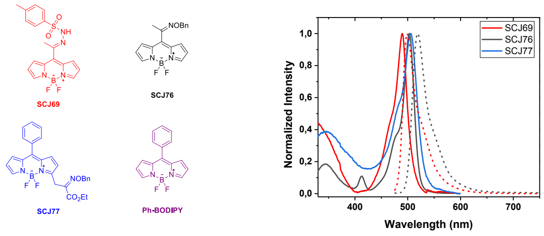
Enhancing photophysical properties of BODIPYs through oxime and hydrazone functionalization: novel imaging agents

João C.S. Simões[1,*], **Ana Beatriz Pereira**[1], **Diogo Veiga**[1], **Sofia F. Duarte**[1], **Susana Lopes**[1], **Ana Clara B. Rodrigues**[1], **Sérgio J. Seixas de Melo**[1,] **Marta Piñeiro**[1], **Teresa M.V.D. Pinho e Melo**[1]

[1] University of Coimbra, Coimbra Chemistry Centre-Institute of Molecular Sciences and Department of Chemistry, 3004-535 Coimbra, Portugal.
**joao95simoes@gmail.com*

BODIPYs are highly conjugated heterocyclic organic compounds with pertinent photophysical properties. The variation of their main structure, by insertion of specific substituents, contributes to the development of new derivatives with different properties. Our group has developed novel routes for the synthesis and functionalization of dipyrromethanes via nitroso- and azoalkenes chemistry which were used as precursors of new BODIPYs containing an oxime/hydrazone group [1-5]. This aims to model their photophysical properties to improve their application as imaging agents [6]. UV-Visible and fluorescence spectra were performed, and preliminary results showed the functionalization improves their photophysical characteristics, where both the nature and position of substituents are relevant.



	λ_{abs}^{max} (nm)	λ_{F}^{max} (nm)	Φ_F
SCJ77	509	524	0.123
Ph-BODIPY	503	521	0.061

Fig.1. i) Schematic representation of the structure of non- and functionalized BODIPYs with oxime or hydrazone groups; ii) absorption (full line) and fluorescence (dotted line) spectra of SCJ69 (red), SCJ76 (black), and SCJ77 (blue) BODIPYs; Table with $\lambda_{abs}^{max}/\lambda_{F}^{max}$ and fluorescence quantum yield values of non- (Ph-BODIPY) and functionalized BODIPY (SCJ77).

Acknowledgments

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Synthetic access to new indazole derivatives with promising anticancer features

Fatima E. Laghchioua[1,2]*, **M. Eddahmi**[1], **M. Viale**[3], **Nuno M. M. Moura**[2], **M. Amparo F. Faustino**[2], **M, Graça P. M. S. Neves**[2], **E. M. Rakib** [1,4].

[1] Laboratory of Molecular Chemistry, Materials and Catalysis, Faculty of Sciences and Technics, Sultan Moulay Slimane University, Beni-Mellal, BP 523, Morocco
[2] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[3] IRCCS Ospedale Policlinico San Martino, U.O.C. Bioterapie, L.go R. Benzi 10, 16132 Genova, Italy
[4] Higher School of Technology, Sultan Moulay Slimane University, BP 336, Fkih Ben Salah, Morocco
laghchioua@ua.pt

Indazole and its derivatives, as a typical class of aromatic *N*-heterocycles, have generated significant concern in synthetic and medicinal chemistry due to their diverse biological activities [1-3]. Our research team has previously developed the synthesis of several indazoles bearing a sulfonamide moiety with good antiproliferative activities [4-7]. Trying to develop potent and selective anticancer agents, a series of new polysubstituted indazoles (Fig.1) were synthesized and evaluated for their in vitro antiproliferative and apoptotic activities against two selected human cancer cell lines (A2780 and A549). Several compounds showed interesting antiproliferative activity with IC50 ranging from 0.64 to 17µM on both cell lines. The most active indazoles were then tested in different pharmacological dilution conditions, adding five new cell lines (A2780, A549, IMR32, MDA-MB-231 and T47D) as targets, confirming their antiproliferative activity.

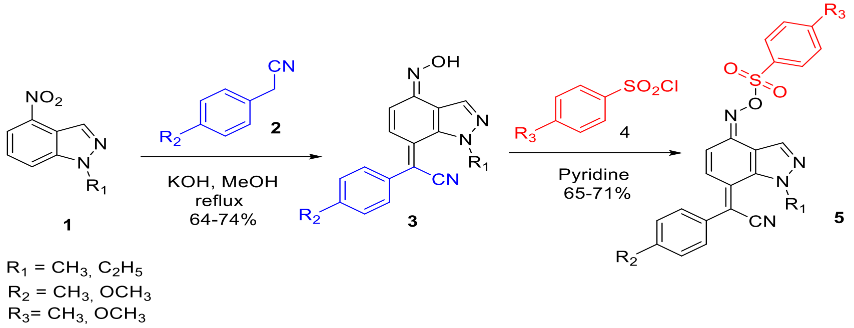

Fig.1. Synthetic strategy to obtain polysubstituted indazoles

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POLYSACCHARIDES FROM MARINE SOURCES: SYNTHESIS OF DERIVATIVES AND TUMOR CELL GROWTH INHIBITION

Rita Lima[1,2], Flávia Barbosa[3,4], Odília Queirós[3], Maria Elizabeth Tiritan[1,2,4], Madalena M. M. Pinto[1,2], Carla Fernandes[1,2*]

[1] Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2] Centro Interdisciplinar de Investigação Marinho e Ambiental (CIIMAR), Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal
[3] UNIPRO - Oral Pathology and Rehabilitation Research Unit, University Institute of Health Sciences (IUCS), CESPU, 4585-116 Gandra, Portugal.
[4] TOXRUN – Toxicology Research Unit, University Institute of Health Sciences Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal
** Correspondent author: cfernandes@ff.up.pt; Tel.: +35-122-042-8688*

Chitosan is a very versatile marine derived polysaccharide considering its flexibility in terms of chemical modifications and coupling methods, which give rise to very promising derivatives and conjugates and improvements in the physicochemical properties and, consequently, in the biological activities [1]. The diversity of biological activities and applications of this polymer is vast and covers a wide range of fields [2]. Although in recent years there has been a large increase in new derivatives and applications [3, 4], there is still much to explore regarding to chitosan as new challenges are always emerging.

This work describes the synthesis of a series of chitosan derivatives obtained through a coupling method involving the formation of a Schiff base between chitosan and diverse bioactive small molecules. The structure elucidation of the synthesized conjugates was established by spectroscopic methods, and elemental analysis. The obtained conjugates were tested for the inhibition of the growth of the human tumor cell lines, A375-C5 (melanoma), MCF-7 (breast adenocarcinoma), and NCI-H460 (non-small cell lung cancer). Considering the biological activity evaluation, one derivative demonstrated promising results, with GI_{50} values lower than 6.83 ± 0.90 for all cell lines.

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Synthesis of fumiquinazoline analogues with antibacterial, anti-biofilm and efflux pump inhibition potential

<u>Mariana C. Almeida</u> [1, 2], Nikoletta Szemerédi [3], Fernando Durães [1, 2], Diana I. S. P. Resende [1, 2,*], Paulo M. da Costa [2,4], Madalena Pinto [1, 2], Gabriella Spengler [3], Emília Sousa [1, 2,*]

[1]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, FFUP – Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313, Porto, Portugal.
[2]CIIMAR – Centro Interdisciplinar de Investigação Marinha e Ambiental, Terminal de Cruzeiros do Porto de Leixões, 4450-208, Matosinhos, Portugal
[3]Department of Medical Microbiology, Albert Szent-Gyorgyi Health Center and Albert Szent-Gyorgyi Medical School, University of Szeged, Semmelweis utca 6, 6725 Szeged, Hungary.
[4]ICBAS – Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313, Porto, Portugal.
dresende@ff.up.pt, esousa@ff.up.pt

Antimicrobial resistance has reached worrisome levels globally [1]. Thus, the development of new compounds that are active against resistant bacterial pathogens is a priority. The overexpression of efflux pumps and the formation of biofilms are some of the most common resistance mechanisms in bacteria and therefore the search for molecules that can counteract them also constitutes a relevant strategy [2]. Fumiquinazolines and related alkaloids constitute a chemical family of compounds with privileged structures and have exhibited numerous bioactivities [3]. In our group, previous work has shown that both natural and synthetic derivatives can exhibit promising antibacterial activities [4, 5].

Herein, several new fumiquinazoline analogues and two naturally-occurring compounds were synthesized through a multi-step pathway [6]. Structure elucidation was accomplished through nuclear magnetic resonance techniques (NMR) and high-resolution mass spectrometry (HRMS). The synthesized compounds were screened for their antibacterial potential and several derivatives showed promising activities against Gram-positive bacteria, including against resistant strains of *Staphylococcus aureus* and *Enterococcus faecalis*. Furthermore, some of the synthesized alkaloids showed potential to act as bacterial efflux pump inhibitors in the ethidium bromide accumulation assay as well as with promising anti-biofilm capacity putting forward this class as new antibacterial agents.

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Exploring the reactivity of a commercial diketopyrrolopyrrole

Vítor A. S. Almodôvar[1*], Augusto C. Tomé[1]

[1] LAQV-Requimte, Department of Chemistry, University of Aveiro, 3810-193 Aveiro,
Portugal.
**email: v.almodovar@ua.pt*

Diketopyrrolopyrroles (DPP) represent a class of brilliant red and strongly fluorescent high-performance pigments that have exceptional light, heat, and environmental stability [1,2].

The synthetic versatility of diaryl DPP is immense. These compounds possess several reactive centers that can be attacked by nucleophiles or electrophiles. This fact allows their chemical transformation into derivatives with improved performance or novel applications [1,3].

This work presents a series of new diketopyrrolopyrrole derivatives synthesized from a cheap commercial DPP (Pigment red 254) [4]. The structures of all new compounds were confirmed by several spectroscopic techniques and their photophysical properties were evaluated.

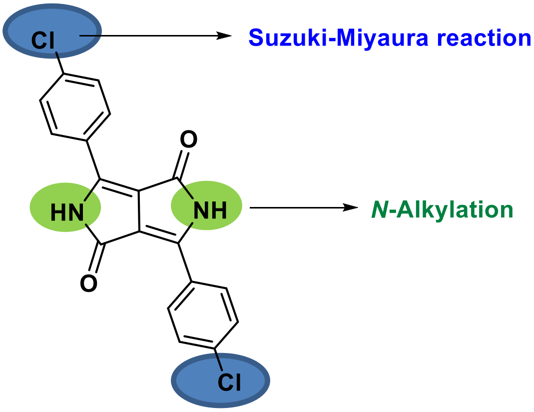

Fig.1. Pigment red 254

Acknowledgments:
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New porphyrins for dye-sensitized solar cells

Ana F. R. Cerqueira[1,*], Ana Lúcia Pinto[2], Maria G.P.M.S. Neves[1], A. Jorge Parola[2], Augusto C. Tomé[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
*anacerqueira@ua.pt

During the last decade, we have seen an increasing scientific interest for dye-sensitized solar cells (DSSCs) due to their efficiency on the harvesting and conversion of sunlight into electricity, their simplicity of production and their low cost [1,2]. In fact, these devices are becoming an alternative to the silicon-based solar cells used today. DSSCs require a photostable organic dye that absorbs much of the visible light. Porphyrin derivatives have shown promising results as dyes for DSSCs with energy conversion efficiencies (PCE) of ca 13% [3].

In this communication, we will report the synthetic strategy to obtain new electron-donor porphyrins, some of them bearing fused rings. The structural characterization and the photovoltaic properties of some of these compounds will also be presented and discussed.

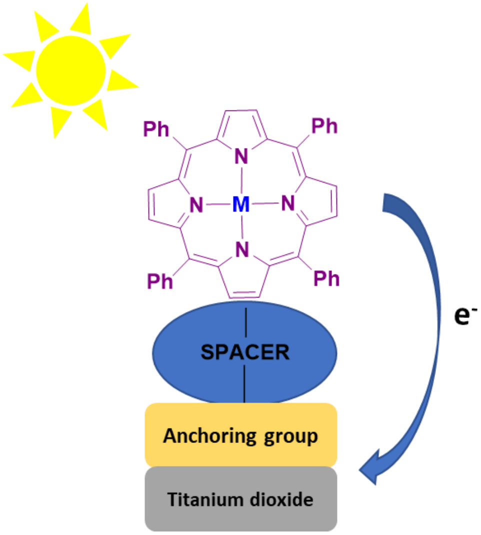

Fig.1. Schematic representation of DSSCs.

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Mild synthesis of nitrobenzenes from 3-formylchromones

Telmo N. Francisco[1,*], **Joana L. C. Sousa**[1], **Samuel Guieu**[1,2], **Artur M. S. Silva**[1], **Hélio M. T. Albuquerque**[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**telmofrancisco@ua.pt*

The synthesis of nitrobenzenes has been explored in the production of multiple chemicals such as dyes, perfumes, and pharmaceutical products. The traditional methods for the synthesis of nitrobenzenes revolve around the electrophilic aromatic nitration of arenes using the "mixed acid" methodology with nitric acid and sulphuric acid [1]. Alternatives strategies include the direct oxidation of anilines [2] or the *ipso*-nitration of aryl and heteroaryl precursors, allowing the preparation of multiple substituted nitro derivatives [3]. Unfortunately, these methods deal with extremely harsh conditions, creating environmental concerns, especially when used in industry for the large-scale production of nitro group-containing compounds, or they need to use transition-metals leading to the formation of undesired waste. Therefore, the search for milder approaches for the synthesis of nitrobenzenes is of upmost importance either laboratory or industrial applications.

Hence, in the present work we explored the use of 3-formylchromones as Michael acceptors, which upon the use of nitromethane as Michael donor allowed for the one-pot formation of three new C—C bonds, which ultimately allowed the synthesis of 3,5-disubstituted nitrobenzenes over very mild reaction conditions. The nitrobenzene compounds were obtained in 52-86% isolated yields (Figure 1) and the method was confirmed to be functional in a gram-scale protocol [4]. The reaction conditions, mechanism, scope and structural analysis, both from NMR and X-Ray, will be presented and discussed.

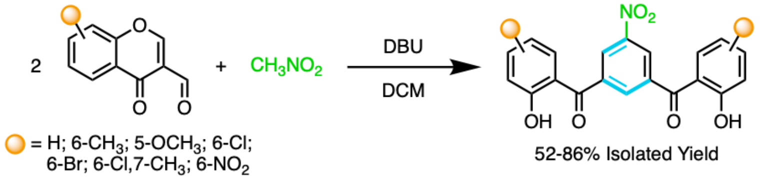

Fig.1. Proposed method for the synthesis of 3,5-disubstituted nitrobenzenes.

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QO16

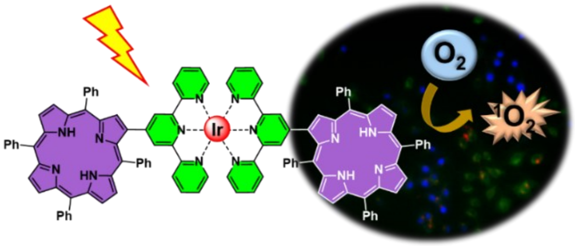
Ru(III) and Ir(III) complexes bearing porphyrin moieties: synthesis and photosensitizing activity against resistant melanoma cells

Nuno M. M. Moura[1,*], Kelly A. D. F. Castro[2], Carlos Lodeiro[3], Maria A. F. Faustino[1], Mário M. Q. Simões[1], Maria G. P. M. S. Neves[1]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
[2] Department of Biomolecular Sciences, Faculty of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo, SP, Brazil
[3] BIOSCOPE Group, LAQV-REQUIMTE, Nova School of Science and Technology, NOVA University Lisbon, Caparica Campus, 2829-516, Caparica, Portugal. ProteoMass Scientific Society, Madan Parque, Rua dos Inventores, 2825-182, Caparica, Portugal
* nmoura@ua.pt

Transition metal complexes (TMCs) emerged as a research area of considerable importance and are receiving much attention from the scientific community owing to their potential application in different fields [1]. In the last years, ruthenium- and iridium-based compounds have emerged as attractive alternatives to platinum-based drugs due to their improved properties [2]. The physicochemical features displayed by tetrapyrrolic macrocycles, namely *meso*-tetraarylporphyrins render them particularly appealing to be used in a wide range of fields such as supramolecular chemistry, catalysis, electronic materials, sensors, and medicine [3], namely as photosensitizers (PS) in photodynamic therapy (PDT) [4]. PDT arises as a promising alternative to the most common therapeutic procedures used against oncological and non-oncological disorders. This is a non-invasive, localized, and low-cost approach, with high selectivity for tumor cells, that requires the use of a PS, which will react with dioxygen when light-activated at a specific wavelength, generating reactive oxygen species (ROS), namely singlet oxygen ($^1O_2$) [5].

Herein, we report the preparation of symmetrical and unsymmetrical ruthenium and iridium complexes of β-functionalized porphyrin derivatives bearing terpyridine ligand units. The combination of porphyrin derivatives with iridium(III) or ruthenium(III) ions induces singular features and, consequently, allow the improvement of the PDT effect of these molecules as PS against B16F10 cells [6].



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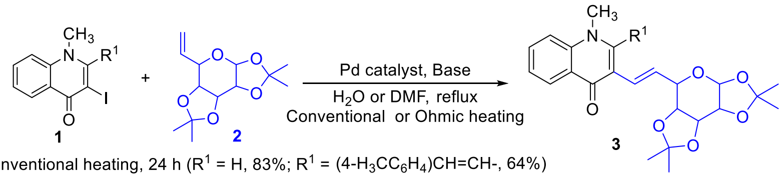
Ohmic heating-assisted palladium-catalyzed cross-coupling reactions for the synthesis of *C*-glycosylquinolones

Pedro M. O. Gomes[1], **Raquel G. Soengas**[2], **Artur M. S. Silva**[1], **Paula B. Andrade**[3], **Vera L. M. Silva**[1]

[1]LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal. [2]Department of Organic and Inorganic Chemistry, University of Oviedo, Julián Clavería 7, 33006 Oviedo, Spain.
[3]LAQV-REQUIMTE, Laboratório de Farmacognosia, Departamento de Química, Faculdade de Farmácia, Universidade do Porto, R. Jorge Viterbo Ferreira, nº 228, 4050-313 Porto, Portugal.
Email: pm.gomes@ua.pt

Quinolin-4(1*H*)-ones (or 4-quinolones), which are very well-known as antibiotics, have a remarkable ability to target type II eukaryotic topoisomerases, being also regarded as promising anticancer compounds [1]. In turn, carbohydrates play a key role in cell recognition processes important in a variety of biological functions, including anticancer activity [2]. The combination of these two pharmacophores in a single molecule, such as *C*-glycosylquinolin-4(1*H*)-ones, seems to be a smart strategy to develop novel anticancer quinolones with improved selectivity for the cancer cells. We envisioned that *C*-glycosyl quinolin-4(1*H*)-ones could be synthesized by palladium(Pd)-catalyzed Heck reaction of a iodinated quinolin-4(1*H*)-one **1** with a sugar alkene **2** (Fig. 1). In fact, Pd-catalyzed cross-coupling reactions are one of the most powerful and popular methods for the formation of carbon–carbon bonds [3].The importance of these reactions has driven chemists to explore alternative procedures, some of them truly game-changing, dramatically accelerating development in this field.

In our group we have been using ohmic heating to promote Pd-catalyzed reactions with success. In this thermal processing method, an alternating electrical current of high frequency crosses a conductive reaction medium, by using electrodes in direct contact with the medium, which is heated by Joule effect, A fast, volumetric and uniform *in situ* heating is achieved leading, in many cases, to an increase of the overall reaction kinetics, selectivity and yields [4]. In this work, we aim to use ohmic heating to develop a more sustainable methodology for the synthesis of *C*-glycosylquinolones **3** using more benign reaction media and heterogeneous catalysis conditions. To achive this goal novel 3-iodoquinolin-4(1*H*)-ones **1** were synthesized following a well-established procedure [5]. In paralell, the vinylsugar **2** was synthesized by the Dess-Martin periodinane (DMP) oxidation of the comercial alcohol to the aldehyde and subsequent Wittig reaction with methyl triphenylphosphonium bromide salt. Afterward, the Heck reaction of quinolin-4(1*H*)-one **1** with the vinylsugar **2** was studied primarily in conventional heating and then in ohmic heating for comparison of both methods and improvement of the methodology towards the development of an efficient protocol for the ohmic heating-assisted synthesis of *C*-glycosylquinolin-4(1*H*)-ones **3** for further studies of their anticancer activity. More details about the experiments performed and obtained results will be presented and discussed in this communication.



Conventional heating, 24 h (R^1 = H, 83%; R^1 = (4-$H_3CC_6H_4$)CH=CH-, 64%)
Ohmic heating, 0.5-1 h (R^1 = H, 45%; R^1 = (4-$H_3CC_6H_4$)CH=CH-, 35%)

Fig.1. Pd-catalyzed Heck reaction of for the synthesis of *C*-glycosylquinolin-4(1*H*)-ones **3**.

Funding
This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

Acknowledgements
Pedro M.O. Gomes thanks FCT/MCTES (Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) and ESF (European Social Fund) through NORTE 2020 (Programa Operacional Região Norte) for his PhD grant 2020.04972.BD. Vera L.M. Silva thanks FCT for funding through the Scientific Employment Stimulus – Institutional Call (Ref. CEECINST/ 00026/ 2018).

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Irá a inteligência artificial assumir o papel do Químico? Um estudo de caso com a reação carbonilativa de Suzuki

J. X. Soares[1,2,3], A. Dias[1], D. R. P. Loureiro[1,2,3], M. M. M. Pinto[2,3], T. Rodrigues[4], C. M. M. Afonso[2,3#*]

[1]Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal.
[2]Interdisciplinary Centre of Marine and Environmental Research (CIIMAR/CIMAR), Porto, Portugal.
[3]LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal.
[4]Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto 1649-003, Lisboa, Portugal
**cafonso@ff.up.pt*

dedicado pelo autor à memoria do Professor Costa Lima

O desenho de uma rota sintética e a otimização de uma reação são processos que tradicionalmente assentam, em boa parte, na intuição do Químico. A intuição, apesar de ser uma ferramenta fundamental, é influenciada pela experiência pessoal e tende a não ser bem sucedida com reações complexas e multifatoriais [1]. Recentemente, algoritmos de inteligência artificial têm sido aplicados com sucesso na análise retrossintética [2], na previsão dos produtos de reação [3] e na otimização de parâmetros reacionais [4].

Neste trabalho, a síntese da 4-metoxixantona foi planeada e otimizada com o auxílio de dois métodos de inteligência artificial. Um dos métodos, baseado no processamento de linguagem natural, foi utilizado para a análise retrossintética e escolha da síntese da substância de interesse. Com base nestes resultados, o acoplamento carbonilativo de Suzuki foi selecionado para a síntese laboratorial da 4-metoxixantona. Nesta reação, o iodofenol é acoplado a um ácido borónico, na presença de atmosfera de CO e de um catalisador organometálico. O outro método, baseado em aprendizagem ativa onde ao longo de um processo iterativo previsões e dados experimentais são conjugados de forma a encontrar as melhores condições experimentais, foi utilizado para a otimização dos parâmetros da reação carbonilativa. O modelo de inteligência artificial desenvolvido e aqui apresentado permitiu obter a 4-metoxixantonanuma única reação (70 %), por oposição ao processo clássico (13 %) que envolve quatro passos reacionais e condições ecologicamente menos sustentáveis. Este é mais um exemplo em que os métodos computacionais permitiram ajudar a intuição do Químico de forma a obter rotas sintéticas mais eficientes e sustentáveis.

Agradecimientos

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QO19

Synthesis and characterization of porphyrins bearing electronic donating groups at *meso*-positions to be used as hole-transporting materials in perovskite solar cells

Melani J. A. Reis[1*], Nuno M. M. Moura[1], Maria Graça P. M. S. Neves[1], Adélio Mendes[2,3], Ana M. V. M. Pereira[2,3]

[1]Department of Chemistry & LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal, [2]ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, [3]LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
**e-mail: melani@ua.pt*

In recent decades, the search for alternative energy sources to fossil fuels is of worldwide concern, due to the increased use of these non-renewable sources, as well as their negative impact on climate change.[1]

Perovskite solar cells (PSCs, **Fig. 1**) play an important and promising role in photovoltaic technologies and could be a good alternative to traditional silicon-based solar cells.[2] During technological evolution, the use of solid-state hole-transporting materials (HTMs) was rapidly explored, and spiro-OMeTAD was selected as the benchmark. However, the synthesis of this HTM has some disadvantages such as high production costs due to a laborious and complex multistep synthetic route in combination with the difficult purification process.[2]

Porphyrins are tetrapyrrolic macrocycles that have great potential as HTMs for PSCs. Due their attractive physicochemical features, namely, high electronic delocalization together with electronic transfer capacity, thermal stability, and high light absorption ability in a wide range of the visible spectrum, have allowed the fabrication of porphyrin-based PSCs with a power conversion efficiency (PCE) of *ca*. 20%.[3,4]

In this communication, we report synthetic routes to achieve novel porphyrin-based derivatives containing nitrogen-donor moieties in *meso*-positions, as well as some of the promising results obtained in evaluating their performance as HTMs in PSC devices.

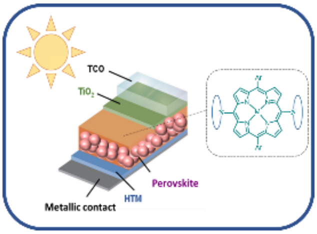

Fig.1. Structure of a PSC device.

Acknowledgements

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QO20

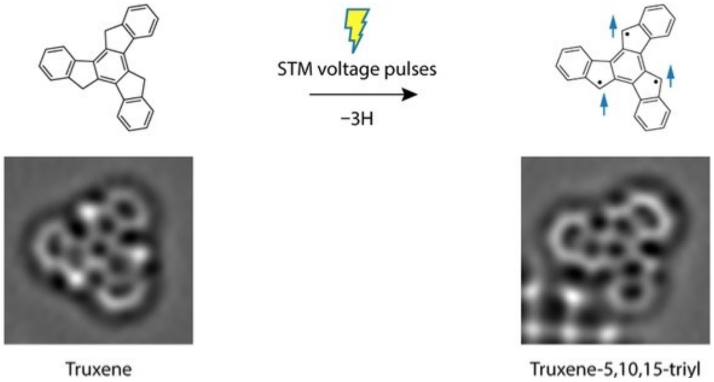
Preparation of Open-Shell Polycyclic Conjugated Hydrocarbons based on Truxene

Saleta Fernández[1*], Shantanu Mishra,[2] Shadi Fatayer,[2] Katharina Kaiser,[2] Diego Peña,[1] Leo Gross.[2]

[1]Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CiQUS) and Departamento de Química Orgánica, Universidad de Santiago de Compostela
C/Jenaro de la Fuente s/n, 15782, Santiago de Compostela
[2]IBM Research-Zurich, 8803 Rüschlikon, Switzerland
*saletafernandez.castro@usc.es

Polycyclic conjugated hydrocarbons (PCHs) have emerged as an important family of molecules for investigating structure-property relationships and emergent phenomena in organic materials. Most notably, certain PCHs, owing to their molecular topology, can exhibit an open-shell ground state, which makes them highly attractive for applications in molecular electronics, spintronics and nonlinear optics.[1-2] However, given the high reactivity of open-shell PCHs, their synthesis in solution is remarkably complex. For that reason, on-surface synthesis under ultrahigh vacuum conditions has gained attention since it allows the generation and characterization of open-shell PCHs on solid surfaces.

In this communication, we report the synthesis and characterization of a nonbenzoid PCH with triradical character, truxene-5,10,15-triyl, combining in-solution synthesis of truxene and its dehydrogenation on surface, by voltage pulses of a combined scanning tunneling microscope (STM) and atomic force microscope (AFM) (Figure 1).[3]



Truxene

Truxene-5,10,15-triyl

Fig.1. AFM images of truxene and the corresponding triradical, truxene-5,10,15-triyl

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Towards the synthesis of large acenes, starphenes, and closely related structures

Luis M. Mateo[1,*], Javier Besteiro-Saez[1], Fátima García[1], Saleta Fernández[1], Enrique Guitián[1], Dolores Pérez[1] and Diego Peña[1]

[1]Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CIQUS), Universidad de Santiago de Compostela, C/ Jenaro de la Fuente s/n, 15782, Santiago de Compostela, Spain
**luismanuel.mateo@usc.es*

Acenes are a class of polycyclic aromatic hydrocarbons (PAHs) that consist of linearly fused benzene rings (Fig. 1a).[1] As a consequence of their unique ring fusion topology, acenes present a low energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap). While this renders the acenes highly relevant for their application in optoelectronics and spintronics, it also leads to severe stability issues, which makes long acenes (*i.e.*, heptacene and beyond) elusive for purely solution-based approaches. Using a combined in-solution and on-surface approach, decacene and dodecacene (the latter being the longest acene reported to this date) were successfully prepared from appropriately designed endoxyacene precursors.[2,3]

Furthermore, our research is focused on a closely related class of compounds, the starphenes. This star-shaped class of nanographenes conceptually consist of three acene "branches" that are fused by one single benzene ring. Starphenes possess higher stability than the acenes, but their purely solution-based synthesis is limited to [10]starphene. For larger analogues (e.g., [13]starphene and [16]starphene), combined in-solution and on-surface strategies have recently been reported.[4] Herein, we will discuss the preparation of the largest starphenes, namely [19]starphenes (Fig. 1b).

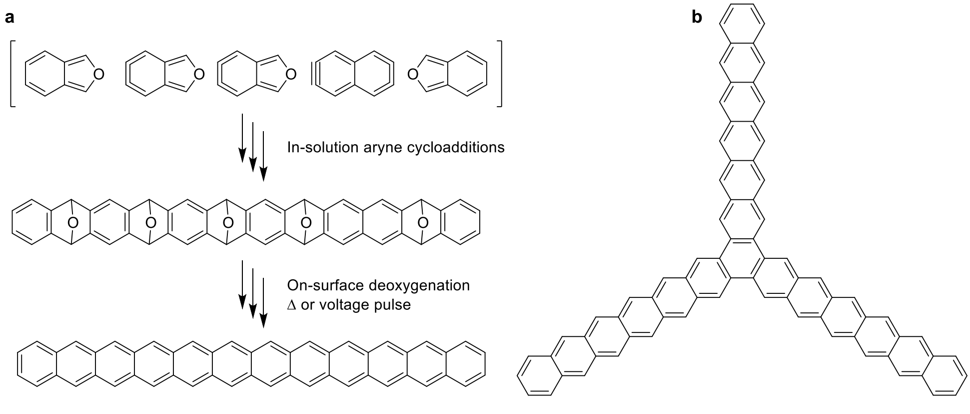

Fig.1. Chemical structure of **a)** the molecular building blocks, decacene and dodecacene, respectively, and **c)** [19]starphene.

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Synthesis of Soluble Trigonal Nanographenes by Pd-catalyzed Aryne Cyclotrimerization

<u>Juan P. Mora-Fuentes</u>,[1] Adrián Martínez-Castrillón,[1] Enrique Guitián,[1] Dolores Pérez,[1] Diego Peña.[1]

[1] Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CiQUS)
and Departamento de Química Orgánica, Universidad de Santiago de Compostela
C/Jenaro de la Fuente s/n, 15782, Santiago de Compostela
juanpedro.mora@usc.es

The study of atomically precise nanographenes (NGs) is crucial to fully exploit their potential applications since their properties are highly dependent on structural variables such as width, length, edge structure, and heteroatom doping. Recently, several approaches based on aryne chemistry have been reported for the preparation of well-defined NGs by chemical methods.1, 2, In this work, we present the synthesis and characterization of novel soluble trigonal NGs (Figure 1). This synthetic strategy is based on Pd-catalyzed [2 + 2 + 2] cycloaddition or arynes which were generated in situ from soluble precursors. In addition, the high solubility of these trigonal NGs in organic solvents at room temperature allowed their purification by chromatographic methods, followed by a complete structural, optoelectronic, and electrochemical characterization.

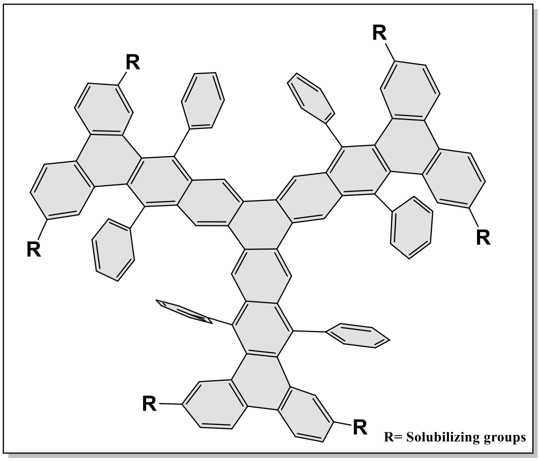

Fig.1. Chemical structure of trigonal nanographenes.

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Synthesis of new porphyrin–fullerene conjugates for application in dye-sensitized solar cells

Vanessa Macedo[1,*], Augusto C. Tomé[1]

[1]LAQV-Requimte, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**vmacedo@ua.pt*

The conversion of solar energy into a profitable energy source, either in the form of organic fuel or electricity, has made a lot of progress, but solar technologies still prove to be quite inefficient, giving rise to the search for more efficient processes.[1]

Porphyrins are compounds exhibit an outstanding light-harvesting ability and are good electron donors. In turn, fullerenes have structural and redox properties that make them excellent electron acceptors. The conjugation of the characteristics of these two compounds, forming porphyrin–fullerene conjugates, demonstrate a great interest to be used in electron transfer processes. Porphyrin–fullerene conjugates have attracted great interest due to their ability to mimic natural photosynthesis through photoinduced charge separation processes.[2-4]

In this communication, we describe the synthesis of new porphyrin–fullerene systems. The new conjugates (**Fig. 1**) were prepared by 1,3-dipolar cycloaddition reactions following a procedure developed in our laboratory.[5]

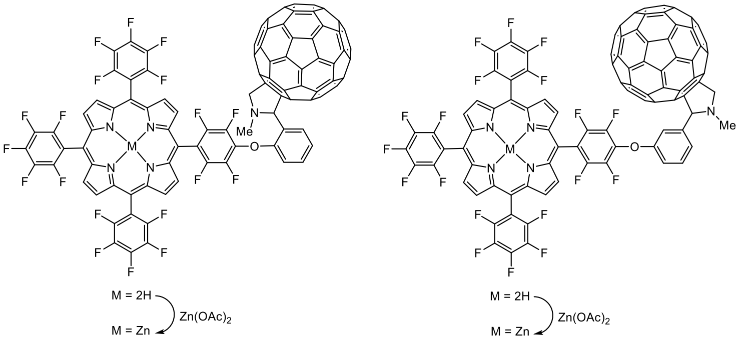

Fig. 1. Structure of the new porphyrin–fullerene conjugates.

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QO24

α-Substituted 2-benzylchromones as monoamine oxidase inhibitors for the treatment of neurological disorders

Vasco F. Batista[1,*], Diana C.G.A. Pinto[1], Artur M. S. Silva[1]

[1]LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3010-093 Aveiro, Portugal
**vfb@ua.pt*

4H-Chromen-4-ones are widely available in both nature and synthetic chemistry, holding relevant pharmacological properties. This template has been at the foundation of drug discovery, leading to treatments for diabetes, inflammation, neurological diseases, and others. In fact, 2- and 3-substituted chromones are great reversible monoamine oxidase inhibitors for treating Parkinson's disease and Depression. [1,2]

Despite extensive research in the field, 2-alkyl chromones remain relatively unexplored due to the difficulty of their synthesis and functionalization. In this work, we report the synthesis and α-functionalization of substituted 2-benzylchromen-*4H*-ones. 2-benzylchromones were synthesized from 2'-hydroxyacetophenone via Claisen condensation and converted to 2-(diazobenzyl)chromones through diazo transfer.[3] These compounds were subjected to a variety of diazo insertion reactions to obtain novel derivatives containing amine, cyclopropane, azine and other functional groups.

Using a fluorimetric assay, a vast library of compounds was then tested for their ability to inhibit human MAO-A and MAO-B. Several compounds showed low micromolar and sub-micromolar IC_{50} values for either MAO-A or MAO-B, with sometimes good selectivity. This activity varied greatly with the substituents introduced, allowing for a SAR study. These results were rationalized through protein-ligand docking studies with crystallographic models of these enzymes containing reversible inhibitors.

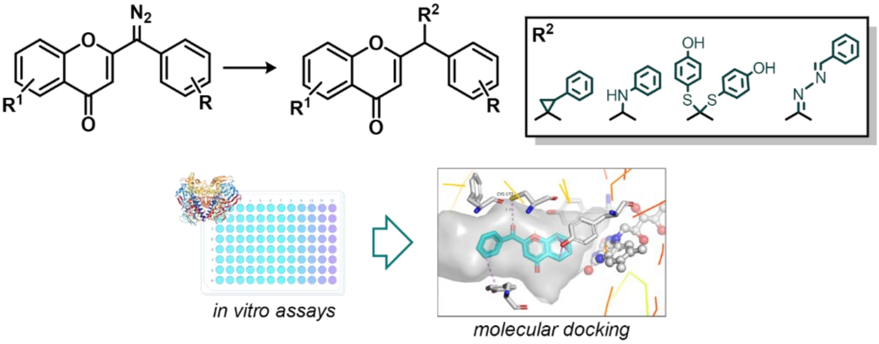

Fig.1. Synthesis of 2-benzylchromone derivatives and their MAO inhibitory activity.

Agradecimentos

This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020. Thanks are due to the Portuguese NMR Network. Vasco F. Batista also thanks FCT for his PhD grant (PD/BD/135099/2017).

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QUÍMICA Y SALUD

Mining the *Leishmania* Kinome

Exequiel O. J. Porta[*], **Karunakaran Kalesh, and Patrick G. Steel.**

Department of Chemistry, Durham University, Durham, DH1 3LE, United Kingdom.
* *exequiel.o.porta@durham.ac.uk*

With >12M of the world's poorest people infected and an economic cost best estimated by >3M disability adjusted life years, the global health challenge represented by leishmaniasis is huge. This challenge is heightened by the fact that the few efficacious drugs available are difficult to administer and often exhibit serious, potentially fatal, side-effects and are also subject to growing resistance. Consequently, the discovery and validation of well-characterised targets to underpin future drug discovery programmes is essential.

Activity-based protein profiling (ABPP) has become a powerful tool for exploring the proteome based on protein chemical reactivity.[1] In the simplest description, this involves the synthesis of molecules containing reactive functional groups (warheads) that have the ability of separating and purifying proteins. In this project, we aimed to develop and explore options to target *Leishmania* kinases through the design, synthesis, and application of five different kinase targeting probes. Kinases are responsible for the regulation of many biological functions and have been targeted for many other indications notably cancer. Consequently, there may be existing drugs with proven efficacy and safety profiles that we can repurpose to radically shorten the time and cost required to bring new drugs to the clinic.

Using an in-house library of new kinase probes, robust workflows have been established to elucidate the *Leishmania* kinome. Details of this, together with studies exploring protein identification and quantification, competitive ABPP experiments and quantitative proteomics mass spectrometry (MS) analyses will be described. These approaches allowed us to establish a landscape of the chemically modifiable *Leishmania* kinome to enable comparison with genetic and proteomic studies undertaken elsewhere. Likewise, these results were used to generate a screening platform for the search for new antileishmanial compounds as inhibitors of selected kinase

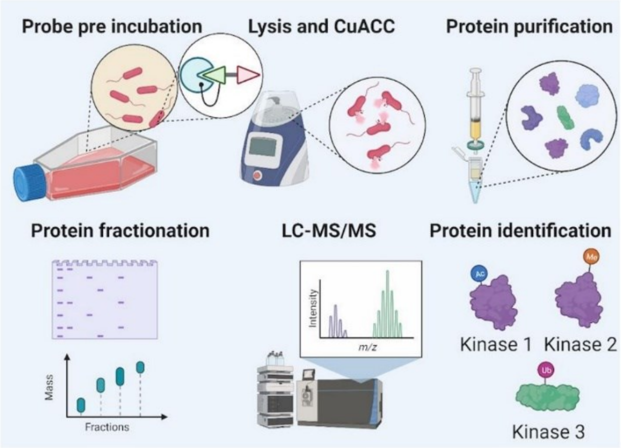

Fig.1. Our ABPP workflow.

Agradecimientos
We thank Institute of Cancer Research (ICR) for help with proteomic experiments.

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O receptor da vitamina D como unha nova diana para o tratamento do cancro de mama

Uxía Gómez-Bouzó[1]*, Hugo Santalla[1], Generosa Gómez[1], Yagamare Fall[1]

[1]Departamento de Química Orgánica e Instituto de Investigación Sanitaria Galicia Sur (IISGS),
Universidade de Vigo, Campus Lagoas-Marcosende, Vigo, España
*ugomez@uvigo.es

O cancro de mama é un dos cancros máis diagnosticados e unha das principais causas de mortalidade por esta doenza. A pesar de mellorar o tratamento con quimioterapia, é necesario atopar novas terapias dirixidas ao bloqueo do crecemento e a propagación deste tipo de cancro. Consecuentemente, estanse a realizar varios estudos para o desenvolvemento de novos fármacos co obxectivo de superar a resistencia.

A forma activa da vitamina D demostrou ter actividade antiproliferativa, pro-apoptótica e antiangioxénica en numerosos estudos preclínicos e en moitos tipos de tumores diferentes. A investigación nesta área céntrase no deseño racional de novos análogos para a obtención de compostos máis potentes e coa esperanza de reducir a propensión a causar efectos tóxicos por hipercalcemia [1].

Daquela, sintetizamos un novo análogo da vitamina D tipo Gemini chamado **UVB1** que ten potentes efectos antitumorais sobre unha ampla gama de liñas celulares tumorais e carece de actividade hipercalcémica. Os resultados obtidos reforzan o seu uso potencial como axente antitumoral para tratar carcinomas colorrectais e de mama [2].

Recentemente, deseñouse un novo análogo do **UVB1** co fin de inducir importantes melloras no seu comportamento como ligando biolóxico. Este novo análogo (**UVB2**) mostra centros quirais adicionais, o que supón un gran desafío para realizar a súa síntese total (Figura 1).

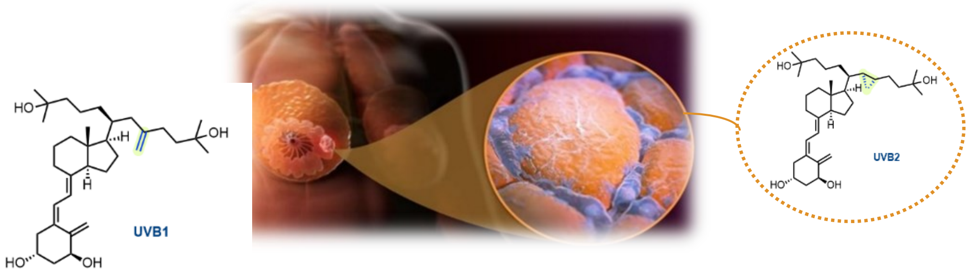

Fig.1. Estrutura dos análogos **UVB1** e **UVB2**.

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The Reaction Mechanism of SARS-CoV-2 Spike Protein Cleavage by TMPRSS2: A Quantum Mechanics/Molecular Mechanics Study

Luís M. C. Teixeira[1], João T. S. Coimbra[1], Maria João Ramos[1], Pedro A. Fernandes[1*]

[1]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências Universidade do
Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
**corresponding author: pafernan@fc.up.pt*

Since COVID-19 was declared an international pandemic, several efforts have been made to control the spread of the SARS-CoV-2 virus. Nowadays, despite the development of vaccines against the virus, there is still an urgent need to develop efficient drugs to treat infected patients. Thus, understanding the biological mechanisms that govern viral infection is essential as it can be helpful in the development of novel therapeutic drugs [1]. An attractive drug target is the transmembrane protease serine 2 (TMPRSS2), a physiological enzyme that plays a vital role in the SARS-CoV-2 infection mechanism. TMPRSS2 promotes a proteolytic cleavage on SARS-CoV-2 Spike (S) protein, culminating in a required conformational change that facilitates host-cell entry [2]. Having in mind that the information retrieved from quantum mechanics/molecular mechanics (QM/MM) studies could be important in the design of transition-state (TS) analogues inhibitors, we used multiscale QM/MM calculations to the determine the mechanism behind the rate-limiting acylation stage of the proteolytic cleavage of the S protein. Our calculations showed that acylation occurred in two sequential steps: i) a nucleophilic attack from Ser441 to the substrate's P1-Arg concerted with a proton transfer to His296, and 2) a proton transfer from His296 to the Substrate's P1'-Ser concerted with the cleavage of the P1-P1' peptide bond. The two steps had a Gibbs activation energy of 17.1 kcal/mol and 15.8 kcal/mol, respectively (**Fig.1)**. An oxyanion hole stabilized the rate-limiting TS by 8 kcal/mol. An analysis of the interactions present at the tetrahedral intermediate pointed out specific ways to construct higher-affinity non-covalent transition-state analogue inhibitors with the potential to be used as therapeutics against SARS-CoV-2.

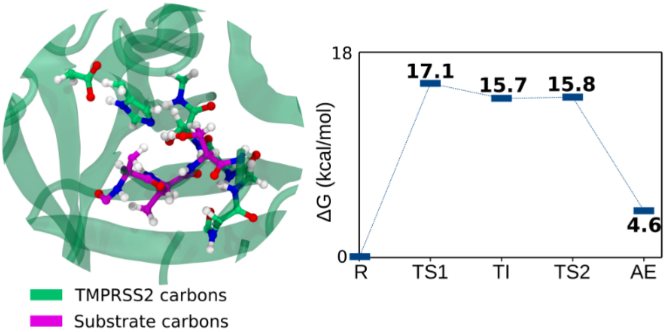

Fig.1. On the left, we depict the atoms of the QM region in sticks and coloured by atom type. The TMPRSS2 carbon atoms are coloured in green, whereas the substrate's carbon atoms are coloured in magenta. On the right, we show the free energy profile for the acylation step catalysed by TMPRSS2 (R, Reagents; TS, Transition-State; TI, Tetrahedral Intermediate; AE, Acyl-Enzyme).

Acknowledgements

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Melanostatin Aza-Peptides as Potent Allosteric Modulators of the Dopamine D₂ Receptors

<u>Xavier C. Correia</u>[1], Ivo E. Sampaio-Dias[1,*], Sara C. Silva-Reis[1,2], Hugo F. Costa-Almeida[1], Vera M. Costa[2,3], Xerardo García-Mera[4], José E. Rodríguez-Borges[1]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2]UCIBIO/REQUIMTE, Laboratory of Toxicology, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[3]Associate Laboratory i4HB – Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4]Department of Organic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Praza do Seminario de Estudos Galegos, 15705 Santiago de Compostela, Spain.
idias@fc.up.pt

Parkinson's disease (PD) is a serious neurologic condition of the central nervous system affecting millions of people worldwide that results in motor and non-motor function disabilities, ultimately leading to death.[1] The gold standard of PD therapy focuses on the potentiation of dopamine in the central nervous system upon the administration of levodopa and inhibitors of dopamine-degrading enzymes.[1] However, long-term therapy with levodopa results in serious adverse effects that can worsen the condition of the disease.[1] Melanostatin (**Fig. 1**) is an endogenous neuropeptide that acts as a positive allosteric modulator (PAM) of the dopamine D_2 receptors and has shown the potential to be used as an alternative PD therapy in clinical studies.[2] However, this peptide fails to exhibit adequate pharmacokinetic properties due to its chemical nature, hampering its clinical use.[2]

In this work, the synthesis and pharmacological evaluation of an aza-analogue of Melanostatin (**Fig. 1**) are described by the incorporation of aza-proline as a proline surrogate, which is expected to exhibit increased chemical and biochemical stability due to poorer enzymatic recognition.[3] This novel aza-analogue was evaluated by pharmacological and biological assays and has demonstrated promising pharmacological properties by decreasing the EC_{50} of dopamine up to 4 times, denoting better performance than the parent neuropeptide at 1 nM (**Fig. 1**). In addition, this aza-peptide did not reveal relevant cytotoxicity at 100 µM, a much higher concentration than its PAM activity denoting a safe therapeutical window. As such, this project is expected to further push forward the knowledge about Melanostatin neuropeptide, paving the way for the development of novel anti-Parkinson hits.

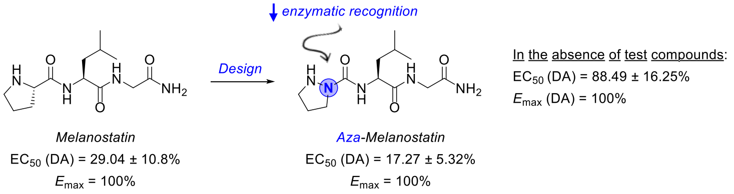

Fig.1. Melanostatin and its aza-analogue (Aza-Melanostatin); potency (EC_{50}) and efficacy (E_{max}) of dopamine (DA) in the presence (1 nM) and in the absence of test compounds.

Funding: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e a Tecnologia, and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020.

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Discovery of Melanostatin-Based Potent Modulators of the Dopamine D_2 Receptors Using Furoic Acids as Proline Surrogates

Ivo E. Sampaio-Dias[1,*], **Sara C. Silva-Reis**[1,2], **Xerardo García-Mera**[3], **Vera M. Costa**[2,4], **José E. Rodríguez-Borges**[1]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]UCIBIO/REQUIMTE, Laboratório de Toxicologia, Faculdade de Farmácia, Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[3]Departament of Organic Chemistry, Faculty of Pharmacy, University of Santago de Compostela, Praza do Seminario de Estudos Galegos, 15705 Santiago de Compostela, Spain.
[4]Associate Laboratory i4HB – Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
**idias@fc.up.pt*

The control of Parkinson's disease (PD) is challenged by motor and non-motor fluctuations as well as dyskinesias associated with levodopa long-term therapy.[1] As such, pharmacological alternatives to reduce reliance on this drug are an unmet medical need. Melanostatin (MIF-1, Fig.1) is a short neuropeptide that acts as a positive allosteric modulator (PAM) of D_2 receptors (D_2R), thereby enhancing the affinity of these receptors towards dopamine, requiring lower doses of levodopa when used in co-therapy as demonstrated in clinical assays.[1,2] Despite its anti-Parkinson potential, MIF-1 displays low stability in CNS tissues and reduced gastrointestinal permeability.[1]

To tackle the disfavourable pharmacokinetic profile associated with MIF-1, a series of 16 analogs were designed, synthesized, and pharmacologically evaluated using 2- and 3-furoic acids as proline surrogates.[1,2] Amongst this series, methyl 3-furoyl-L-leucylglycinate and 3-furoyl-L-leucylglycinamide (**I** and **II**, respectively, Fig.1) displayed potent PAM activity and D_2-selectivity.[1] Structure-activity relationship analysis shows that the 3-furoyl scaffold is an adequate bioisostere and that the C-terminal carboxamide moiety is crucial to enhancing the potency and toxicological profile (as found in **II**), yet it is not considered a requisite for the PAM activity.[1] Conformational analysis excludes **I** from adopting the claimed bioactive type II β-turn.[1] The validation of **II** as a lead compound opens a new avenue for the development of a novel class of anti-Parkinson therapeutics targeting the D_2R.

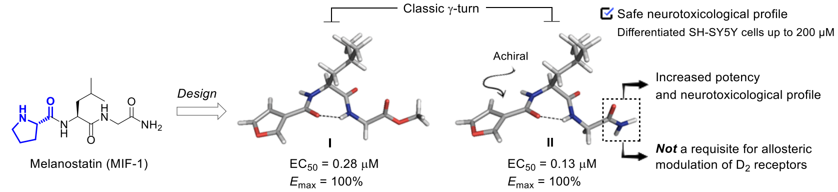

Fig.1. Melanostatin neuropeptide and furoyl-based analogs with potent PAM activity and D_2 selectivity.

Funding

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Uma Abordagem Bioisostérica na Descoberta de Potentes Análogos da Melanostatina Usando β-Aminoácidos

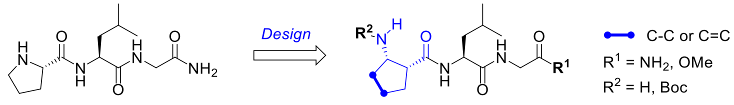
Costa-Almeida, H. F.[1]; Sampaio-Dias, I. E.[1,*]; Silva-Reis, S. C.[1,2]; Correia, X. C.[1]; Costa, V. M.[2,3]; Carvalho, F.[2,3]; García-Mera, X.[4]; Rodríguez-Borges, J. E.[1]

[1]LAQV/REQUIMTE, Departamento de Quimica e Bioquimica, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre 1021 1055, 4169-007 Porto, Portugal.
[2]UCIBIO/REQUIMTE, Laboratório de Toxicologia, Faculdade de Farmácia, Universidade do Porto , R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[3]Associate Laboratory i4HB, Institute for Health and Bioeconomy, Faculdade de Farmácia, Universidade do Porto , R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4]Departamento de Química Orgánica, Facultad de Farmacia, Universidad Santiago de Compostela, Praza do Seminario de Estudos Galegos, 15705 Santiago de Compostela, Spain.
**email: idias@fc.up.pt*

A Melanostatina (MIF-1) é um tripéptido endógeno hipotalâmico (Pro-Leu-Gly-NH_2) com diversas funções no sistema nervoso central. Este neuropéptido é reconhecido principalmente pela sua atividade como modulador alostérico positivo (MAP) dos recetores de dopamina do tipo D_2 (D_2R).[1] Pode por isso, ter aplicações biomédicas em doenças neurológicas como a doença de Parkinson (DP). Os MAP são uma classe de ligandos que, aquando da sua ligação ao local alostérico, induzem mudanças conformacionais nos recetores-alvo resultando num aumento de afinidade para os ligandos ortostérios. Esta classe apresenta diversas vantagens em comparação com fármacos do tipo ortostéricos, como alta especificidade e efeitos secundários limitados.

Apesar do seu inegável potencial farmacológico no tratamento da DP, em ensaios clínicos a MIF-1 apresenta propriedades farmacocinéticas desfavoráveis tal como baixa biodisponibilidade gastrointestinal e alta labilidade para proteases. Neste trabalho, pretende-se ultrapassar esses problemas farmacocinéticos sem comprometer a sua atividade como MAP através de uma abordagem bioisostérica. Para o efeito, o resíduo da prolina deste neuropéptido foi substituído por β-aminoácidos de forma a aumentar a resistência à proteólise e melhorar a permeabilidade celular.

Neste contexto, seis novos prolinomiméticos da MIF-1 contendo β-amino ácidos cíclicos foram sintetizados e avaliados farmacologicamente mediante ensaios funcionais em D_2R. Um dos análogos sintetizados potencia o efeito da dopamina até 2,5 vezes mais do que a MIF-1 a 1 nM. Além disso, não foi observada citotoxicidade para este composto até 100 μM em células neuronais SH-SY5Y diferenciadas. Estudos adicionais estão a ser realizados para determinar a estabilidade química e bioquímica deste novo análogo e a sua permeabilidade celular em modelos *in vitro*. A descoberta de novos MAP seletivos e potentes dos D_2R com perfil citotóxico seguro abrirá portas à descoberta de novos compostos *hit* e ao desenvolvimento de terapias complementares contra o Parkinson.



Melanostatina (MIF-1) **Peptidomiméticos da MIF-1**

Fig.1. Estrutura da MIF-1 e análogos sintetizados contendo β-amino ácidos.

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QS07

Bio-guided optimization of *Cystoseira abies-marina* cosmeceuticals extraction by advanced technologies

Gonçalo P. Rosa[1,2,], Andreia F. Peixoto[3], Ana M. L. Seca[1,2] , M. Carmo Barreto[2], Diana C. G. A. Pinto[3]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro
[2]cE3c- Centre for Ecology, Evolution and Environmental Changes, Azorean Biodiversity Group, CHANGE – Global Change and Sustainability Institute, Faculty of Sciences and Technology, University of the Azores
[3]LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto
**goncalo.p.rosa@ua.pt*

Seaweeds are a great source of unique secondary metabolites, presenting activity against various conditions like cancer, neurodegenerative diseases and metabolic syndrome, among others. In addition, seaweeds are very attractive for cosmetic applications due to their antioxidant, anti-inflammatory, and immune-modelling properties [1].

Cystoseira abies-marina is a brown seaweed species presenting interesting anti-tumor, anti-inflammatory and antioxidant activities, but no records of anti-aging activities have been found [2], making it an excellent candidate to evaluate its cosmetical potential.

Ultrasound- (UAE) and microwave-assisted extraction (MAE) are advanced sustainable technologies which have been found to be very efficient in enhancing bioactive compounds extraction [3].

In this regard, *Cystoseira abies-marina* extracts were prepared by UAE and MAE with varying conditions of solvent, time and algae/solvent ratio, and the antiaging activities of the extracts were assessed, to determine which conditions yielded a higher cosmeceutical potential.

The data obtained was autoscaled (z-score), and further analyzed through hierarchical clustering, and factor analysis of mixed data (FAMD). The statistical analysis showed that, in general, UAE extracts had higher yields than those obtained by MAE. Ethyl acetate proved to be the best solvent for UAE in both yield of extraction and biological activities, while ethanol led to better results in MAE. Shorter extraction times yielded more active extracts with UAE, while the influence of this condition was not so marked on MAE. Antioxidant activities were better in MAE when compared with the UAE extracts, but the latter presented higher anti-tyrosinase and anti-elastase activities.

This approach not only enables the bio-guided optimization of the extraction process towards its cosmeceutical potential but also grants the ability to modulate an extract's activity by changing the extraction conditions according to the target.

Acknowledgements

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New synthetic cinnamic acid-flavone hybrids with promising photoprotective, anti-inflammatory and antioxidant activities

Ana Jesus [1,2], Joana Gomes [3,4], Joana Moreira [3,4], Gonçalo Brites [5,6], Madalena Pinto [3,4], Maria T. Cruz [5,6], Honorina Cidade[3,4,*], Isabel F. Almeida [1,2,*]

[1] Associate Laboratory i4HB—Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto,4050-313 Porto, Portugal;
[2] UCIBIO—Applied Molecular Biosciences Unit, MedTech, Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[3] CIIMAR—Interdisciplinary Centre of Marine and Environmental Research, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal;
[4] Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal;
[5] Faculty of Pharmacy, University of Coimbra, 3004-531 Coimbra, Portugal;
[6] Centre for Innovative Biomedicine and Biotechnology (CIBB) and Center for Neuroscience and Cell Biology - CNC, 3004-504 Coimbra, Portugal
** hcidade@ff.up.pt and ifalmeida@ff.up.pt*

It is known that oxidative stress contributes for the development of skin inflammatory pathologies, including atopic and contact dermatitis, psoriasis, and skin cancer [1]. UV radiation is recognized as one of the main triggers for the generation of reactive oxygen (ROS) and nitrogen (RNS) species. Sunscreens containing UV filters and antioxidants have been proposed as a strategy to prevent skin damage mediated by UV-induced ROS and RNS [2,3]. In recent years, the interest concerning new multifunctional compounds, especially natural and nature-derived, has increased due to the minimalist skin care trend focused on reducing environmental footprint [4,5].

Flavonoids and cinnamic acids, widely found in nature, display antioxidant and anti-inflammatory activities [5], and have been used as an inspiration for development of new synthetic hybrids with promising health effects [6]. Aiming the discovery of new multifunctional compounds to fight the negative impact of solar radiation, cinnamic acid-flavonoid hybrids were herein prepared. A total of seven hybrids, containing flavone and cinnamic acid moieties connected by amide and/or ester linkers, were synthetized and characterized by nuclear magnetic resonance (NMR) spectroscopy.

Their cytotoxicity was evaluated in two cell lines representing the epidermis and dermis, namely keratinocytes and macrophages, respectively, using resazurin assay, and their anti-inflammatory activity was accessed in a macrophage cell line. All the seven compounds afforded cell viability higher than 70% in the range of concentrations tested. Five of the seven hybrids revealed interesting inhibitory activity (between 40-80%) towards the production of nitric oxide (NO) in LPS-stimulated cells. Among all the compounds, three of them revealed ability to absorb in UVA range (UVA/UVB ratio > 1), and one of them also displayed potential to be a broad-spectrum UV filter (critical wavelength ≥ 370 nm). In the future, we intend to evaluate the antioxidant activity and the photo-reactivity of the most promising compounds, aiming the development of multifunctional sunscreens.

Acknowledgments:

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New insights into the anti-inflammatory effects of 2-stryrylchromones

Mariana Lucas[1,*], Marisa Freitas[1], Artur M. S. Silva[2], Eduarda Fernandes[1], Daniela Ribeiro[1,3]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal

[2]LAQV, REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

[3]Faculty of Agrarian Sciences and Environment, University of the Azores, 9700-042 Angra do Heroísmo, Açores, Portugal

**up201912326@edu.ff.up.pt*

Neutrophils, during the inflammatory response, in a process known as oxidative burst, increase oxygen consumption, causing an elevated production of reactive pro-oxidant species (RPS). This excessive production can activate several signaling pathways and different cellular responses, such as increasing the release of arachidonic acid and consequently the production of prostaglandins (PG) by cyclooxygenases (COX). COX inducible isoform, COX-2, is predominantly expressed and upregulated in inflammatory cells during inflammation [1]. Thereby, the overproduction of RPS and PG are important events that lead to the amplification of the inflammatory condition. Thus, it is important to find molecules that can act on these processes to regulate the inflammatory response. 2-styrylchromones (2-SC) belong to the chromone family and have a styryl moiety linked at C-2 of the chromone core and their anti-inflammatory properties are scarcely demonstrated in the available literature [2]. Therefore, in this work, the impact of a panel of twenty-one 2-SC on the modulation of the oxidative burst in freshly isolated human neutrophils was evaluated by a chemiluminescent method [3]. Additionally, to evaluate the effect of 2-SC on COX-2 activity two assays were conducted: a colorimetric detection of PGE_2 production in human whole blood, and a fluorometric detection of PGG_2 production through an *in vitro* assay with the isolated human recombinant COX-2 [4].

Focusing on the substituents present on B-ring of the tested 2-SC, they were divided into 4 groups: group A, without any substitution on B-ring; group B, with a OH at C-4'; group C, with a catechol group (C-3' and C-4') and group D, with a OCH_3 at C-4'. The 2-SC from group C were the most active in the modulation of the neutrophils' oxidative burst and in the direct inhibition of COX-2. In the human blood assay, the most active 2-SC belongs to group D. Thus, the presence of the catechol group on B-ring seems to favor the modulation of neutrophils' oxidative burst and the inhibition of isolated COX-2, and for this last one the presence of a OH at C-8 on A-ring also appears to play an important role for the activity. Contrariwise, the inhibition of PGE_2 production in the blood assay appears to be influenced by the presence of a OCH_3 at C-4' on B-ring. Finally, some of the studied 2-SC were able to modulate more than one of the studied pathways which may be beneficial, since they may act through more than one mechanism of action and more effectively regulate the inflammatory response.

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Pyrroloquinolone-based hybrid compounds multitargeting the electron transport chain of *Mycobacterium tuberculosis*

M. Clariano[1,*], **D. Nunes**[1], **D. Canudo**[1], **M. J. Perry**[1], **F. Lopes**[1]

[1]Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Lisbon, Portugal
**martaclariano@campus.ul.pt*

Tuberculosis (TB), caused by *Mycobacterium tuberculosis* (Mtb), is the second world's deadliest infectious disease, only after COVID-19 [1]. TB is still an uncontrolled disease, representing a significant public health concern, mainly due to the long duration of the treatments, patient noncompliance and to the development and spread of multidrug and extensively drug resistant TB [2]. Additionally, the available anti-TB drugs do not address the latent forms, prevalent in 90 % of infected people. If the immune system is compromised these latent forms can become active and contagious. Thus, it is essential the discovery of novel molecular structures and the development of new drugs with potent activity against drug resistant replicant and latent Mtb [2].

Mtb's viability depends on the energy produced by its respiratory chain. Combination of compounds targeting different components of the electron transport chain (ETC) has been considered as an innovative and potentially successful approach to avoid the emergence of resistance [3].

Our aim is to progress a set of pyrroloquinolones (PYQ), that arose from a screening against Mtb H37Rv strain, into viable lead candidates. These compounds are developed to multitarget the ETC of Mtb, through the inhibition of cytochrome *bcc* while simultaneously releasing nitric oxide, tackling both the active and latent forms of Mtb. Here we present the synthetic strategy to obtain a small library of cytochrome *bcc* inhibitors and hybrid compounds. To expand the library of PYQ, we diversify the linker between the PYQ core and the substituents at **R** position (**Fig. 1**). Biological evaluation against Mtb H37Rv strain as well as solubility determination will also be presented.

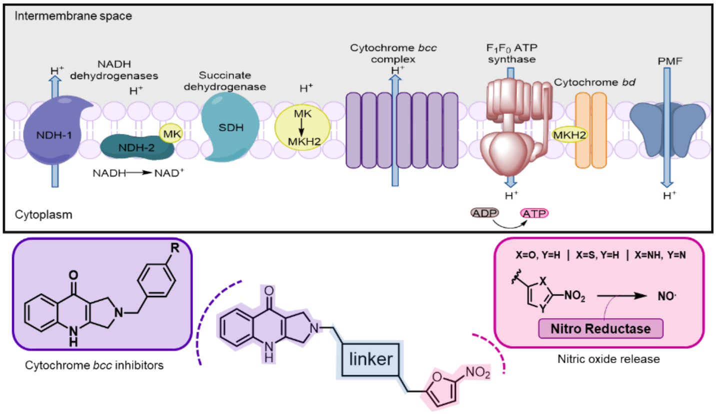

Fig.1. Pyrroloquinolones multitargeting the electron transport chain of *Mycobacterium tuberculosis*.

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QS11

Recent advances in cancer therapies *via* carbon nanomaterials functionalized with porphyrins and analogues

Ana R. Monteiro[1,2,*], Catarina I. V. Ramos[1], Nuno M. M. Moura[1], Sara Fateixa[2], Leandro M. O. Lourenço[1], Luca Menilli[3,4], Silvia Lazzarotto[4], Filipe M. P. Morais[1], Ana T. P. C. Gomes[5], Joana Rodrigues[6], Maria A. F. Faustino[1], Giorgia Miolo[4], Maria G. P. M. S. Neves[1], Tito Trindade[2]

[1]LAQV-REQUIMTE, Department of Chemistry of University of Aveiro, 3810-193 Aveiro, Portugal
[2]CICECO, Department of Chemistry of University of Aveiro, 3810-193, Aveiro, Portugal.
[3]Department of Biology of University of Padova, 35131 Padova, Italy.
[4]Department of Pharmaceutical and Pharmacological Sciences of University of Padova, 35131 Padova, Italy.
[5]Center for Interdisciplinary Investigation (CIIS), Faculty of Dental Medicine, Universidade Católica Portuguesa, 3504-505 Viseu, Portugal.
[6]i3N, Department of Physics of University of Aveiro, 3810-193 Aveiro, Portugal.
**anarita.rvcm@ua.pt*

Graphene oxide (GO) and graphene quantum dots (GQDs) are carbon nanomaterials with increasing importance as delivery platforms of traditional anticancer drugs [1,2]. Here, we explore some breakthroughs (**A-D**) on the synthesis of new hybrid materials comprising GO/GQDs and photosensitizing molecules (porphyrins or phthalocyanines, Pcs) and their synergistic contributions to conventional cancer therapies, such as photodynamic therapy (PDT) or in deoxyribonucleic acid (DNA) G-quadruplex (G4) sensing and stabilization, as follows:

A: Tetracationic porphyrins (TMPyP, Zn-TMPyP and P1-C_5) were loaded onto GO/GQDs, and their photo-antiproliferative activity was evaluated under red light (625 nm) against T24 human bladder cancer (BC) cells [3]. The hybrids showed a high photodynamic activity, namely Zn-TMPyP@GQDs.

B: Four tetracationic ZnPcs were assembled on GO to develop multifunctional “turn-off-on” G4 sensors [4]. GO induced a re-organization of the ZnPcs mostly to J-aggregates and quenched their original fluorescence, which was then recovered in the presence of G4 [$(T_2G_5T)_4$]. This suggested a progressive release of ZnPcs from GO to detect and stabilize G4 (K_D up to 1.92 μM) over time.

C: GQDs were covalently attached to DNA sequences, shaping their folding properties and generating luminescent GQDs-supported G4, which allow the anchoring of cationic porphyrins, such as TMPyP. These arrays could be potentially used in biosensing or mediated drug delivery processes.

D: New π-expanded porphyrin derivatives containing terpyridine motifs at *meso* positions (tpy-Por) were synthesized and explored to enhance non-covalent interactions of neutral porphyrins with GO and GO functionalized with Au nanoparticles.

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Anti-inflammatory activity of 2-styrylchromones in Human fibroblast like synoviocytes

Ana T. Rufino[1], **Mariana Lucas**[1], **Artur M. S. Silva**[2], **Eduarda Fernandes**[1], **Daniela Ribeiro**[1,3]

[1] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2] LAQV, REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal
3 Faculty of Agrarian Sciences and Environment, University of the Azores, Angra do Heroísmo, Açores, Portugal
**arufino@ff.up.pt*

Rheumatoid arthritis (RA) is a systemic immune and inflammatory long-term disease that leads to the destruction of the joints, for which there is no completely effective treatment. It is characterized by persistent synovial inflammation and irreversible cartilage and bone damage [1]. Despite that, effective drugs that can control synovitis and catabolism and contribute to stop the progression of RA remain an unmet need [2].

2-Styrylchromones (2-SC) are chromone derivatives characterized by the existence of a styryl group in the chromone structure. Natural and synthetic 2-SC have been demonstrated to have interesting biological activities, including antioxidant and anti-inflammatory activities [3]. Thus, 2-SC may be considered interesting candidates for the search of new and effective compounds for RA treatment.

The present study investigated the effect of a set of six structurally related 2-SC on IL1β-challenged human fibroblast-like synoviocytes. It was studied their effects on the increased levels of •NO, iNOS, pointing the role of NF-κB activation in the process. It was also evaluated the protein levels of the catabolic protein MMP-3 and the levels of COX-2 for their role on the degradation of bone and cartilage and inflammatory process, respectively.

From the hydroxy and methoxylated 2-SC tested, the one presenting two methoxy substituents at C-5 and C-7 of A ring and a catechol group on B ring, significantly reduced iNOS and MMP-3 protein expression and •NO production. This same 2-SC also inhibited the NF-κB pathway by reversing the IL-1β-induced levels of cytoplasmatic IκBα and decreasing the p65 nuclear levels, suggesting the involvement of these pathways in the observed iNOS and MMP-3 levels. Nevertheless, in the same conditions, the COX-2 levels increased.

The obtained results are of great value to better understand the anti-inflammatory pathways of 2-SC on RA, highlighting a possible negative feedback loop mechanism of action. These mechanisms should be further explored and carefully evaluated to demonstrate the full potential of 2-SC towards RA.

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Urea derivatives of β-carboline indole alkaloids for reversing multidrug resistance in cancer

F. Barbosa[1*], B. Montsch[2], P. Heffeter[2] and M. J.U. Ferreira[1]

[1]Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal
[2]Center for Cancer Research, Medical University of Vienna, Borschkegasse 8a, 1090 Vienna, Austria
**filipadbarbosa@edu.ulisboa.pt*

The efficacy of cancer treatment has been seriously hindered by the development of multidrug resistance (MDR). One of the most significant mechanisms of MDR is related with the overexpression of the ABC transporter proteins P-glycoprotein (P-gp/ABCB1), multidrug resistance protein (MRP1/ABCC1) and breast cancer resistance protein (BCRP/ABCG2), which act as efflux pumps. Thus, the development of efflux pump inhibitors, able to restore the cytotoxicity of anticancer agents, has been considered a promising approach to address the issue of cancer drug resistance.

Aiming at finding new MDR reversers, a natural β-carboline indole alkaloid was derivatized. A set of new urea derivatives was prepared by reaction with different isocyanates, bearing aliphatic and aromatic moieties, whose structures were determined mainly by 1D and 2D (HMQC and HMBC) NMR experiments.

The compounds were evaluated for their anti-MDR potential, through functional and chemosensitivity assays, in several human sensitive and resistant cancer cells. Firstly, the antiproliferative activity of compounds was evaluated through the 3-(4,5 dimethylthiazol-2-yl)-2,5-diphenylthetrazolium bromide (MTT) viability assay. The best results were found for a derivative bearing a furan moiety. Moreover, this compound showed selective antiproliferative activity toward resistant cancer cells, having collateral sensitivity effect. The ability of the compounds to act as inhibitors of the ABC transporters P-gp and BCRP was also investigated by flow cytometry.

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Evaluation of the cytotoxicity effects of flavonol derivatives in human lung fibroblasts

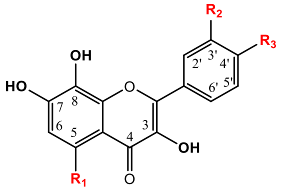
Isabela Santos[*1], **Hélio M. T. Albuquerque**[2], **Artur M. S. Silva**[2], **Eduarda Fernandes**[1], **José Miguel P. Ferreira de Oliveira**[1]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemistry, Campus Universitario de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal
**up202112015@ff.up.pt*

Cancer is the second leading cause of death worldwide [1]. Surgery with chemotherapy and radiation, treatments have limited efficacy or significant adverse effects [2]. Therefore, safer, and more efficient therapeutic agents are essential. Flavonoids, compounds largely found in the human diet, have shown promising cancer-inhibiting properties [3,4]. The cytotoxic effect of flavonoids in human cancer cell lines is widely exploited. Nevertheless, the corresponding effect in healthy human cells is underreported.

The present study aimed to evaluate the toxicity of a group of flavonoids hydroxylated at C-3, C-7, and C-8 in lung fibroblasts. For this, the MRC-5 human lung fibroblast cell line was incubated with flavonoids, 0 – 160 µM, with additional hydroxy groups at C-5, C-3' and/or C-4' or methoxy at C-3' and 4'. After incubation for 48 h, the inhibition of cell viability and growth was measured using the WST-8 and sulforhodamine B assays, respectively.

The presence of 3',4' -methoxy was associated with high cytotoxicity, while the presence of hydroxy groups at C-3'and/or C-4' and C-5 presented low toxicity. Although additional studies are required to ascertain the role of methoxy groups in toxicity, these results reveal that for the studied compounds, methoxy substituted flavonoids presented higher *in vitro* toxicity in healthy human cells than the hydroxy-substituted flavonoids.



F	R
1	R_1, R_2=H; R_3 = OH
2	R_1, R_2, R_3 = OH
3	R_1= H; R_2, R_3 = OCH_3

Fig. 1: Structure of flavonoids tested for its cytotoxic effects in MRC-5 cells.

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QS15

Active Pharmaceutical Ingredient's multicomponent solid forms: a contribution to enhance the trimethoprim biopharmaceutical performance

Giusi Piccirillo[1*], Rafael T. Aroso[1], João A. Baptista[1], João Canotilho[2], Ricardo A. E. Castro[2], Gabriela J. da Silva[2], Mario J. F. Calvete[1], Mariette. M. Pereira[1], M. Ermelinda S. Eusébio[1]

[1] CQC, CQC/IMS, Chemistry Department, University of Coimbra, Rua Larga 3004-535, Coimbra, Portugal
[2] Faculty of Pharmacy, University of Coimbra, 3000-548, Coimbra, Portugal.
** giupiccirillo12@gmail.com*

Antibiotics have been considered one of the most important groups of medicines due to their effectiveness in managing infectious diseases. Their overuse for humans and animals' treatment has led to the development of antimicrobial resistance (AMR) as well as to the accumulation in the environment [1]. This environmental issue is also a common problem for other drugs, such as anti-inflammatories. One of the approaches to reduce AMR issue and the release of disposable Active Pharmaceutical Ingredients (APIs), may be to improve the performance of existing drugs, by decreasing the amount of API normally loaded in pharmaceutical dosage forms through the development of new solid forms (e.g. salts, cocrystals, coamorphous and eutectic mixture) [2]. Thus, new multicomponent solid forms are developed using pharmaceutically acceptable coformers aiming to enhance the solubility/intrinsic dissolution rate of Class II and IV Biopharmaceutical Classification System (BCS) and the antibacterial activity by synergic or additive effect or inhibiting bacterial efflux pumps. Trimethoprim (TMP) is a Class II BCS and the 4th most prescribed antibiotic worldwide [3], normally administrated to treat several bacterial infections, mainly those of the urinary tract [4].

In this communication, we present our achievements in the screening of TMP-based multicomponent forms obtained *via* mechanochemistry, assisted by ethanol, with different co-formers: nicotinic acid (NIC), ibuprofen (IBU), paracetamol (PARA) and CIP (Figure 1). The formation of a salt, a cocrystal, and two eutectic mixtures will be discussed. We present the samples characterization by differential scanning calorimetry (DSC), infrared spectroscopy (IR), and powder X-ray diffraction (PXRD), and their intrinsic dissolution rate assessed as well as the antibacterial assays toward *E. coli* and *S. aureus* carried out to evaluate the effect of TMP in the new associations.

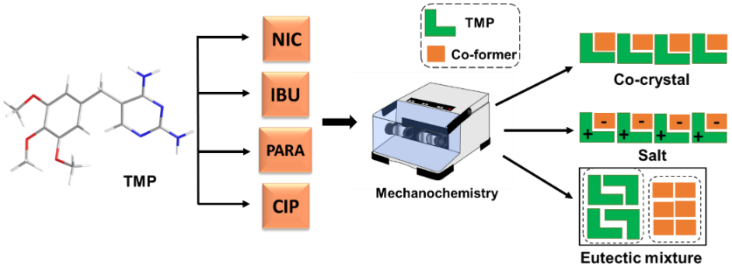

Fig.1. Schematic representation of the TMP-based multicomponent solid forms obtained.

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QS16

Polyhydroxylated *bis*-chalcones: potential new inhibitors of cyclooxygenase 2

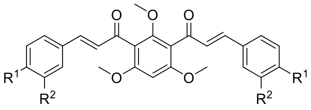
Rui Pereira [1], Mariana Lucas [1], Vera L. M. Silva [2], Artur M. S. Silva [2], Daniela Ribeiro [1,3], Eduarda Fernandes [1]

[1] LAQV-REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal.
[2] LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[3] Faculty of Agrarian Sciences and Environment, University of the Azores, 9700-042 Angra do Heroísmo, Açores, Portugal.
**r97pereira@gmail.com*

Inflammation is a natural reactive response of the organism to infection or injury caused by microbial agents and is regulated by a balance of pro- and anti-inflammatory signals. If this balance is disrupted by the excessive and sustained formation of pro-inflammatory mediators, chronic inflammation may develop. This disorder is associated with diseases such as rheumatoid arthritis, atherosclerosis, tuberculosis, and pulmonary fibrosis [1]. The anti-inflammatory drugs currently available to treat such diseases have many associated side effects, which justify the development of improved therapeutic solutions. Flavonoids are natural compounds that have long been associated as potential alternative drugs with powerful anti-inflammatory effects [2]. More recently, flavonoid precursors such as chalcones have also attracted attention due to their anti-inflammatory activities alongside fewer adverse side effects [2]. However, some new derivatives such as (polyhydroxylated) *bis*-chalcones are less studied. In this context, this work aims the development of an efficient methodology for the synthesis of new *bis*-chalcones and evaluation of their potential as anti-inflammatory compounds.

Herein, we report the synthesis of several *bis*-chalcone derivatives with different substituents, including multiple hydroxy groups, protected and unprotected, halogens and prenyl groups, obtained by basic catalyzed Claisen–Schmidt condensation of *bis*-acetophenones with aromatic aldehydes (table 1). The anti-inflammatory activities of some of the synthesized *bis*-chalcones are also reported. The compounds were submitted to an *in vitro* COX-2 (human recombinant) inhibition assay, using celecoxib as positive control. The results reveal that *bis*-chalcones **3** and **4** were the most active (table 1), leading to the confirmation that the presence of hydroxy groups is the major contributing factor to the inhibition of prostaglandins production, via COX-2.

Table 1. Structure of *bis*-chalcones studied and respective results of the COX-2 inhibition assay

Structure	**Compound**	$\mathbf{R^1}$	$\mathbf{R^2}$	**COX-2 inhibition ± SEM (%), at 100 µM**
	1	OMe	H	< 30
	2	OMe	OMe	< 30
	3	OH	H	47.1 ± 6.8
	4	OH	OMe	80.53 ± 0.6
	5	Br	H	< 30
	6	H	Cl	< 30

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Synthesis of naringenin sulfates and evaluation of their anti-inflammatory activity

T. Macedo[1*], **F. Paiva-Martins[2]**, **P. Valentão[1]**, **D.M. Pereira[1]**

[1]REQUIMTE/LAQV, Laboratório de Farmacognosia, Departamento de Química, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal | [2] REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Porto, Portugal

tiagomgmacedo@gmail.com

Naringenin is a flavanone known for having several pharmacological effects, its anti-inflammatory action being one of the most widely described [1]. Most of the studies on the interference of sulfur groups on the anti-inflammatory of flavonoids suggest that these group affect it negatively [2], however there are conflicting reports on this matter.

In this work we obtained sulfur-containing naringenin derivatives and submitted them to cell-based assessment of anti-inflammatory properties in human macrophages, namely on p65 nuclear translocation (Figure 1), NF-κB activation, and IL-6, TNF-α, and IL-1β production.

The results show that naringenin 4'-*O*-sulfate and naringenin 7-*O*-sulfate exhibit higher activity in comparison with the parent compound naringenin. Naringenin 7-*O*-sulfate was able to reduce IL-6 and TNF-α production by decreasing the translocation of p65. Differently, naringenin 4'-*O*-sulfate decreased the levels of the cytokines without interference on the p65 translocation, pointing to a different mechanism of action. We further compiled a library of several hundred sulfur-containing flavonoids and mapped their chemical space in order to highlight the physico-chemical features of the molecules described here as a strategy to shed a light on their promising anti-inflammatory properties. Even though further investigation is necessary, these results suggest that it is possible to modulate the anti-inflammatory mechanism of action of flavanones through the choice of sulfation patterns.

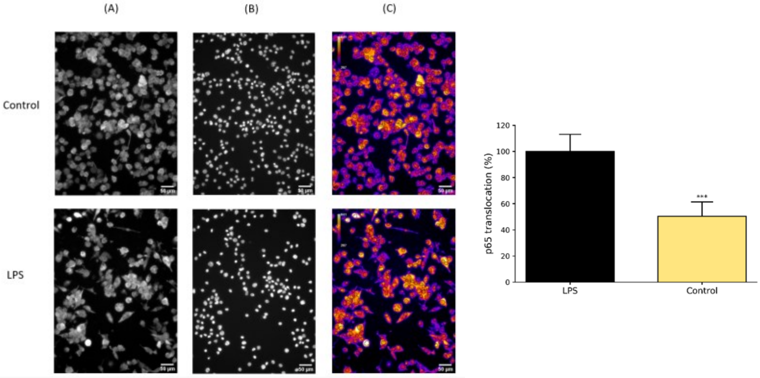

Figure 1 - Immunofluorescence assay with THP-1 differentiated macrophages after antibody staining of cytoplasmic/nuclear p65 (A) and DAPI staining of nuclei (B) with/without LPS stimulation (Control). p65 staining image was overlayed with the outlines of the nucleus stained by DAPI (C).

Funding

This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

Acknowledgements

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QS18

Cationic imidazolyl porphyrins bearing amphiphilic side chains combined with antimicrobials: new strategies to potentiate *E. coli* photodynamic inactivation

Rafael T. Aroso[1,*], Madalena C. Silva[1], Carolina V. Domingos[1], Janusz M. Dabrowski[2], Barbara Pucelik[2], Agata Barzowska[2], Gabriela J. da Silva[3], Rui M. B. Carrilho[1], Luís G. Arnaut[1], Mariette M. Pereira[1]

[1] Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal;
[2] Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387, Krakow, Poland
[3] Faculty of Pharmacy and Center for Neurosciences and Cell Biology, University of Coimbra, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
** rafael.aroso@student.uc.pt*

Nowadays, 1.3 million annual deaths are attributed to multi-drug resistant (MDR) bacterial infections, with up to 100.000 deaths caused by MDR *Escherichia coli*, one of the most problematic microorganisms according to the World Health Organization. Photodynamic inactivation (PDI) has been regarded as an alternative therapy to combat topical MDR bacterial infections, due to its broad antimicrobial activity spectrum and low propensity for inducing resistance development. PDI combines a drug named photosensitizer, light and molecular oxygen, resulting in the production of reactive oxygen species that can destroy bacteria. One of the main issues with PDI monotherapies is the difficulty in eliminating all bacteria present in an infected tissue during light irradiation. After PDI treatment, the remaining live bacteria can proliferate again and lead to a recurrence of the infection. To address this issue, recent reports have highlighted the potential of a synergic combination of PDI with currently available antibiotics (dual therapy).[2]

Herein we present structure-activity studies[3] on the combination of cationic imidazolyl-substituted porphyrin photosensitizers, bearing side chains with different amphiphilic properties, with known antimicrobial agents (e.g. ciprofloxacin and cinnamaldehyde) for inactivation of *E. coli* (Fig. 1). Additional mechanistic studies (photochemical, bacterial uptake and confocal microscopy) were carried out to explain the beneficial effects of the amphiphilic side chains at the photosensitizer on the antimicrobial activity. Overall, a synergic effect on the application of aPDI (cationic imidazolyl porphyrins as photosensitizers) followed by administration of both the antibiotic ciprofloxacin or cinnamaldehyde will be discussed. A clear superiority over their corresponding monotherapies is demonstrated. Both *in vitro* and *in vivo* studies clearly highlight the potential of these alternative dual therapies to lower the probability of bacterial resistance development, which is essential for a sustainable long-term treatment of infectious diseases.

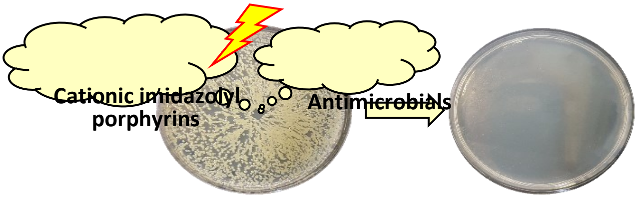

Fig.1. Schematic representation of *E. coli* inactivation using a combination of PDI with antimicrobials.

Acknowledgements

This work was supported by FCT (Fundação para a Ciência e Tecnologia), QREN/FEDER (COMPETE Programa Operacional Factores de Competitividade) through projects UIDB/00313/2020 and PTDC/QUI-OUT/0303/2021. The authors also acknowledge IAPMEI-PRR funding (Produtech R3, 2022) and and UC-Santander for "Prémios Semente de Investigação interdisciplinar" funding (CO2BioFilter).

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QS19

Design of a disposable µPAD for on-hand quantification of urinary creatinine

Maria M. P. Melo*, António O. S. S. Rangel, Raquel B. R. Mesquita

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327 4169-005, Porto, Portugal

**mprodrigues@ucp.pt*

In this work, a new microfluidic paper-based analytical device (µPAD) was developed for on-hand creatinine quantification in urine samples. This is clinically significant since creatinine monitorization in urine is an indicator of health condition, as kidney-failure [1]. When compared with conventional methods, this innovative µPAD approach is more accessible, portable, providing low-cost analysis and applicable to non-invasive biological fluids [2]. Additionally, the µPAD is environmentally friendly, as it uses small amounts of reagents, results in low waste production, and is disposal by incineration.

The developed µPAD configuration consisted in two layers of filter paper discs (9.5 mm of diameter) staked into a hydrophilic unit and aligned into a laminated plastic pouch (hydrophobic zone), with 3 mm holes for the standard/sample insertion. The top layer served as a reservoir and the bottom layer contained the reagent (alkaline picrate). After the standard/sample loading, creatinine reacts with picric acid in alkaline conditions, forming an orange/red complex. The colour was registered by scanning the µPAD and the image processed in ImageJ software to obtain the colour intensity values then used to calculate the absorbance. A linear correlation was established between the creatinine concentration and the calculated absorbance values. The µPAD operational parameters were studied to attain the best sensitivity (calibration curve slope) for creatinine determination within the dynamic range of 2.20 - 35.0 mg/dL with a limit of detection (LOD) of 0.66 mg/dL and a limit of quantification (LOQ) of 2.2 mg/dL.

Finally, the method was validated by analysing several urine samples with the developed µPAD and comparing the results with a comparative batchwise process, and it was demonstrated that there were no statistically significant differences between them.

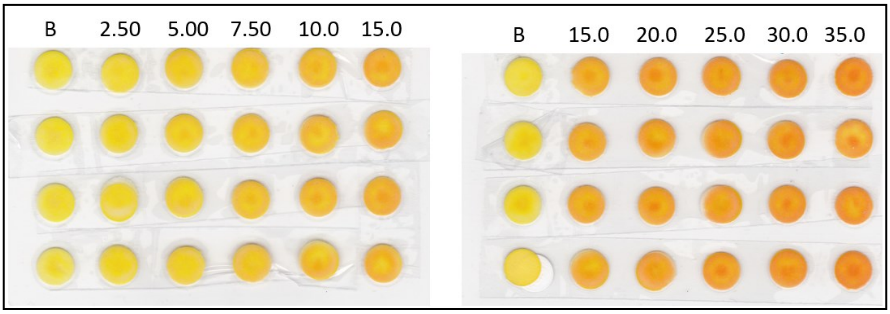

Fig. 3. Scanned images of µPADs after insertion of creatinine standard solutions (in mg/dL); B – blank solution.

Acknowledge

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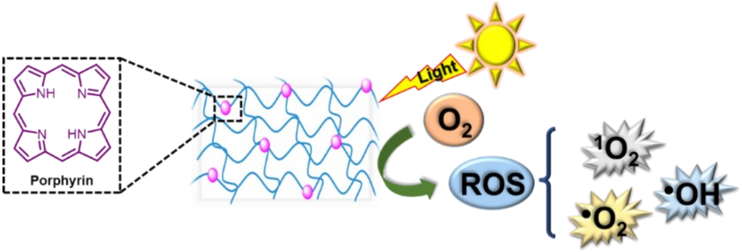
Development of Photoactive Materials for Photodynamic Therapy Based Applications

Nuno M. M. Moura[1], Kelly A.D.F. Castro[1,2], Carla I.M. Santos[1,3], Ana R. Monteiro[1,4], Catarina I. V. Ramos[1], Carlos J. P. Monteiro[1], Adelaide Almeida[5], Ângela Cunha[5], M. Amparo F. Faustino,[1] M. Graça P.M.S. Neves[1*]

[1]LAQV-REQUIMTE, Department of Chemistry of University of Aveiro, 3810-193 Aveiro, Portugal
[2]Laboratory of Bioinorganic and Catalysis, Federal University of Paraná, Department of Chemistry, CP 19081, CEP 81531-990, Curitiba, Paraná, Brazil,
[3]Centro de Química Estrutural, Institute of Molecular Science and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049–001 Lisboa, Portugal
[4]CICECO, Department of Chemistry of University of Aveiro, 3810-193, Aveiro, Portugal
[5]Department of Biology & CESAM, University of Aveiro, 3810-193 Aveiro, Portugal.
*gneves@ua.pt

The possibility of using the photodynamic approaches under clinical but also under non-clinical contexts like improving the microbiological quality of food and water, controlling insect pests, to disinfect and sterilizing surfaces and materials merits special attention of several research groups namely ours [1]. However, the extension of this promising approach to some practical applications requires the immobilization of the photoactive dye in inert solid supports.

In this communication will be discussed some synthetic approaches developed in our group to functionalize *meso*-tetraarylporphyrins and analogues for further immobilization in different supports (e.g. silica, chitosan, titanium oxide, graphene oxide). An insight into the efficacy of the hybrids to photoinactivate microorganisms and their biocompatibility in cells will be also presented [2-5].



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Developing a computer-aided drug design approach to discover lead-like Phosphomannomutase 2 pharmaco-chaperones for congenital disorders of glycosylation (CDG) therapy

Salvador C.M. Magrinho[1,2,3,4]*, Sandra Brasil[2,3,4], Vanessa R. Ferreira[2,3,4], Giuseppina Andreotti[5], Paula A. Videira[2,3,4], Florbela Pereira[1,4]

[1]LAQV-Requimte, NOVA University of Lisbon - School of Science and Technology, Caparica, Portugal
[2]Associate Lab i4HB, Institute for Health and Bioeconomy, NOVA School of Science and Technology
[3]UCIBIO Applied Molecular Biosciences Unit, NOVA School of Science and Technology
[4]CDG & Allies PPAIN, NOVA School of Science and Technology, Caparica Portugal
[5]Istituto di Chimica Biomolecolare, Consiglio Nazionale delle Ricerche, Naples, Italy
**s.magrinho@campus.fct.unl.pt*

Congenital disorders of glycosylation (CDG) are a group of rare diseases caused by inherited defects in cellular glycosylation mechanisms, ultimately leading to a range of multisystem disease phenotypes. The most common, PMM2-CDG, with >1000 reported cases [1], is characterised by genetic defects in phosphomannomutase 2 (PMM2), which catalyses the conversion of mannose 6-P to mannose 1-P, a substrate for posttranslational *N*-glycosylation. While no effective treatment is yet available, previous functional characterisation studies in patient-observed mutations raised the possibility of designing pharmaco-chaperone (PC) therapies to stabilize PMM2 structure and partially rescue its activity [2].

Using an experimentally-validated dataset containing over 10.000 compounds whose interaction with human PMM2, namely thermal stability and IC_{50} (half maximal inhibitory concentration), had been previously assayed, we developed two machine learning strategies to unveil possible PCs for hPMM2 activation: 1) A quantitative structure-activity relationship (QSAR) classification model to predict the interaction of submitted molecules with PMM2 and 2) a QSAR regression model to estimate a theoretical IC_{50} value. These QSAR models served as computational tools to perform a virtual drug screen to search and select molecules with the desired PC profile. Compounds with interesting results were submitted to docking studies to further explore possible protein-ligand interactions.

Promising hits include quinolone derivates, phenylpropanoic acid derivates, vitamins, amongst others. Some of these compounds were acquired and we are currently conducting *in vitro* experiments in patient-derived fibroblast cell lines to analyse their effect on mutant PMM2 activity from cell extracts, as well as lectin-based assays for glycan profiling. This experimental work allows to elaborate on the therapeutic potential of selected hits and will provide proof-of-concept for the applied methodology, defining the models' predictive capabilities for such complex structure-biological activity relationships.

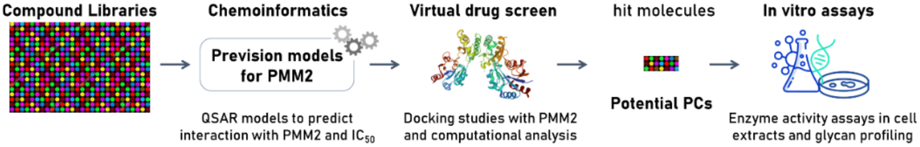

Fig.1. General workflow for the computer-aided drug design methodology.

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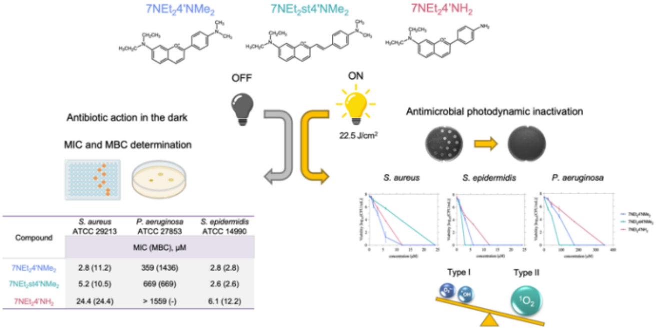
New insights on the antimicrobial properties of amino-based flavylium dyes: promising candidates for photodynamic inactivation of bacteria

Patrícia Correia,[a*] **Paula Araújo**[a], **Ana Rita Pereira**[a], **Lucinda Bessa**[b], **Nuno Mateus**[a], **Victor de Freitas**[a], **Joana Oliveira**[a] **and Iva Fernandes**[a]

[1] REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, 4169-007 Porto, Portugal
[2] Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Egas Moniz – Cooperativa de Ensino Superior CRL, Almada, Portugal
**patricia.correia@fc.up.pt*

The present study aimed to explore the antibacterial activity of a group of nature inspired and structurally similar amino-based flavylium dyes: $7NEt_24'NMe_2$, $7NEt_2st4'NMe_2$, $7NEt_24'NH_2$ and $7NEt_24'OH$. Apart from $7NEt_24'OH$, the other 3 compounds inhibited the growth of Gram-positive (*Staphylococcus aureus* and *Staphylococcus epidermidis*) and Gram-negative (*Pseudomonas aeruginosa*) bacteria, with MIC values in the range of 2.61-24.4 μM and 359-669 μM, respectively. Besides their toxicity in the dark, considerable light-induced killing effects were observed after one single light dose treatment (22.5 J/cm^2). Photoinactivation effect was particularly effective against Gram-positive bacteria, where complete eradication of bacterial growth was achieved at concentrations as low as 12, 6 and 3 μM. Photochemical mechanistic studies suggested the occurrence of both type I (free radicals) and type II (singlet oxygen) reactions, although light-induced damages appear to be predominantly caused by singlet oxygen action.

Taken together, the results herein presented highlight the dual-antibacterial action of this group of molecules, showing antibiotic activity in the dark and photosensitizer behavior under visible light exposure. These findings underline a new application for amino-based flavylium dyes in the management of microbial skin infections.



Compound	*S. aureus* ATCC 29213	*P. aeruginosa* ATCC 27853	*S. epidermidis* ATCC 14990
	MIC (MBC), μM		
$7NEt_24'NMe_2$	2.8 (11.2)	359 (1436)	2.8 (2.8)
$7NEt_2st4'NMe_2$	5.2 (10.5)	669 (669)	2.6 (2.6)
$7NEt_24'NH_2$	24.4 (24.4)	> 1559 (-)	6.1 (12.2)

Fig.1. Schematic representation of aPDI mediated effects of amino-based flavylium dyes.

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Fluorinated contrast agents for application in ^{19}F MRI and PET

Daniela S.S. Teixeira[1*], **Sara M.A. Pinto**[1], **Rafael T. Aroso**[1], **Mariette M. Pereira**[1]

[1]Coimbra Chemistry Center (CQC), Chemistry Department, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
**danielateixeira27@gmail.com*

Early detection of several pathologies, such as coronary[1], neurovascular[2], and tumor diseases[3], has been one of the main strategies adopted in clinical practice to reduce mortality. The design/development of new imaging technologies and high specific/sensible contrast agents (CA) made a high contribution in this direction. Currently, ^{1}H MRI and PET are the imaging technologies most used in clinic. Although, with ^{1}H MRI some artifacts can appear in the generated image due to the high presence of water in the organism, turning more difficult the visualization of the tissues.[4] To overcome this, recently the use of ^{19}F MRI appeared as a prominent strategy, since fluorine is absent in the biological tissues and has similar properties comparatively to proton.[5,6]

Herein, we present the synthesis of new water-soluble manganese fluorinated porphyrins and their evaluation as potential ^{19}F MRI CA. The distance between manganese and fluorine in the porphyrin's structure is a crucial parameter in the optimization of the Mn-induced ^{19}F relaxation rates. The lead manganese porphyrin reveled a substantial reduction of ^{19}F T_1 value from 849 to 15 ms, when compared with the corresponding free base porphyrin. These good relaxivity properties combined with porphyrin's biocompatibility make them promising CA for future use in clinic.

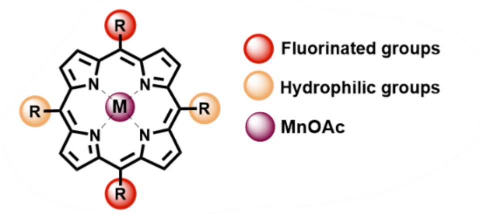

Fig.1. General structure of synthesized CAs.

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New families of multi-target direct ligands for Alzheimer's Disease

Daniela Malafaia[1,*], Ana Oliveira[2], Pedro A. Fernandes[2], Maria J. Ramos[2], Artur M. S. Silva[1], Hélio M. T. Albuquerque[1]

[1]LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]LAQV-REQUIMTE, Computational Biochemistry Laboratory, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal.
*danielamalafaia@ua.pt

The Alzheimer's disease (AD) is a complex multifactorial neurodegenerative disorder, mainly characterized for the progressive and unremitting memory loss and cognitive, motor, and functional capacity [1]. To date, there is no cure or prophylaxis for this neurodegenerative disorder, as the clinically available single-target drugs only provide limited symptomatic treatment and do not alter the course of the disease [2].

Although the exact cause of AD is still unclear, a number of hallmarks are considered crucial for its development, including the β-amyloid (Aβ) and acetylcholinesterase (AChE) [3]. The multifactorial nature of this disease, combined with the consequent identification of many possible targets and target combinations might be intimately related to the consecutive failure in the discovery of new drugs with disease-modifying effects [3].

To address this issue, the multitarget directed ligands (MTDLs) are emerging as a therapeutic alternative to target the multiple AD-related factors [4]. Following this concept, herein we describe the design, synthesis, and biological evaluation of a family of chromeno[3,4-*b*]xanthones as well as their (*E*)-2-[2-(propargyloxy)styryl]chromone precursors, as promising AChE and Aβ aggregation dual-inhibitors for AD [5].

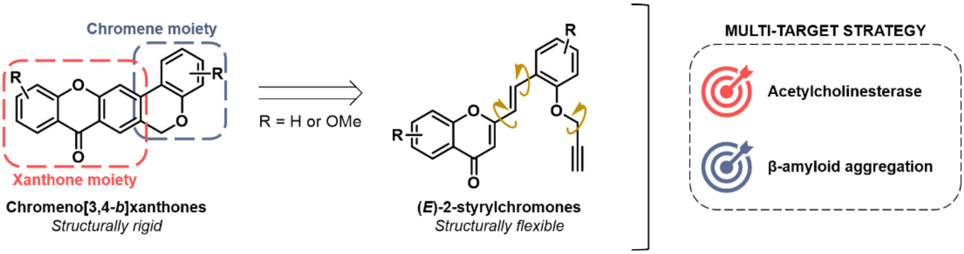

Fig.1. Chromeno[3,4-*b*]xanthones and their structurally flexible precursors as new MTDLs for AD.

Acknowledgements

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Estudo integrado da influência do tipo de cultivo e irrigação nas propriedades bioativas de *Cichorium spinosum* L.

Paschoalinotto B. H.[1,2,3]; Prieto M.A.[3]; Compocholi M.[4]; Polyzos N.[4]; Pires, T.C.S.P.[1,2]; Petropoulos S.A.[4]; Dias M.I.[1,2,*]; Barros L.[1,2]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[3] Grupo de Nutrición y Bromatología, Departamento de Química Analítica e dos Alimentos, Facultade de Ciencia e Tecnoloxía dos Alimentos, Universidade de Vigo, Campus de Ourense, 32004 Ourense, España;
[4] Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 38446 Volos, Greece.
*maria.ines@ipb.pt

Cichorium spinosum L. é uma planta silvestre comestível da bacia do Mediterrâneo, também conhecida como chicória espinhosa, utilizada em receitas e bebidas tradicionais da denominada "*Dieta Mediterrânica*". A procura incessante por produtos naturais benéficos para a saúde renovaram/aumentaram o interesse por espécies de plantas não tão conhecidas e consumidas pelo consumidor, devido sobretudo ao seu perfil fitoquímico e propriedades bioativas de elevado interesse [1]. A par disto, técnicas alternativas de cultivo têm vindo a ser aplicadas para obtenção deste tipo de plantas, sob o estandarte da produtividade sustentável e ecológica, como sendo a hidroponia e a rotação de culturas. Estas práticas podem potencializar a gestão racional da água, a otimização dos regimes de fertilização e, sobretudo, aumentar a adaptabilidade destas plantas silvestres a sistemas controlados de produção [2]. Assim, o presente estudo objetivou a avaliação das propriedades antioxidante (ensaio de TBARS) e antibacteriana (ensaio colorimétrico, isolados clínicos) dos extratos hidroetanólicos das folhas de *C. spinosum* produzidas com irrigação completa ou deficit e com ou sem rotação com uma cultura de milho (CM). Foram ainda usados dois controlos usando água da chuva para irrigação e com e sem rotação com milho.

Relativamente a atividade antioxidante, os extratos com deficit de irrigação combinado com rotação com CM destacaram-se pelo potencial de inibir a peroxidação lipídica, revelando os menores valores de IC_{50}. Não houve diferenças significativas nos extratos com irrigação completa, e os valores menos promissores foram encontrados particularmente nas amostras controlo.

Em geral, as bactérias Gram-positivas demonstraram maior sensibilidade aos extratos hidroetanólicos do controlo sem rotação com CM, seguido dos extratos oriundos da produção com deficit de irrigação e sem rotação de CM. Em particular, a estirpe bacteriana de *Staphylococcus aureus* demonstrou ser a mais sensível de todas as estudas, nomeadamente nas amostras irrigadas com água de chuva e sem rotação com CM (Concentração mínima inibitória de 2.5 mg/mL). Nenhuma das amostras revelou capacidade bactericida.

O estudo integrado permitiu observar que a combinação da irrigação com rotação de cultura de milho afeta significativamente as propriedades bioativas da chicória. Estudos complementares serão necessários para identificar os compostos responsáveis pelas bioatividades assim como otimizar a produção das plantas para obtenção de maiores teores de moléculas de alto valor agregado.

Agradecimentos

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Synthesis of di-imidazolyl porphyrins and their chlorin derivatives for photoinactivation of bacteria and viruses

Zoe A. Arnaut[1,*], **Rafael T. Aroso[1]**, **Sara M. A. Pinto[1]**, **Ana C. S. Lobo[2]**, **Anita S. Amorim[1]**, **Mário J. F. Calvete[1]**, **Paulo Rodrigues-Santos[3,4,5]**, **Dina Pereira[5]**, **Luis P. de Almeida[5]**, **Luis G. Arnaut[1]**, **Mariette M. Pereira[1]**

[1]CQC, Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal
[2]LaserLeap Technologies, R. Col. Júlio Veiga Simão, CTCV, Ed. B, 3025-307 Coimbra, Portugal
[3]Laboratory of Immunology and Oncology, Center for Neuroscience and Cell Biology (CNC), University of Coimbra, Coimbra, Portugal;
[4]Institute of Immunology, Faculty of Medicine (FMUC), University of Coimbra, Coimbra, Portugal
[5]Center for Innovation in Biomedicine and Biotechnology (CIBB), University of Coimbra, Coimbra, Portugal
[6]Center for Neuroscience and Cell Biology (CNC), University of Coimbra, 3004-517 Coimbra, Portugal
**zoearnaut@gmail.com*

The concerns over antimicrobial resistance have risen throughout the past years, leading the scientific community to seek new and alternative therapies to fight microorganisms [1]. From all the potential alternatives, we highlight antimicrobial photodynamic inactivation (aPDI). This innovative treatment uses a photosensitizer, capable of generating reactive oxygen species (ROS), in the presence of light and oxygen, to induce oxidative stress to kill pathogens. Although the principles behind this therapy have been widely used in cancer treatments, their use as antimicrobials is still limited [2,3]. This fact is possibly due to the lack in development of suitable and scalable synthetic methods for preparing ideal photosensitizers, which combine high ROS with selective targeting to cross biofilm barriers, gram-negative bacteria membranes, or virus receptors. Recently, we observed that cationic *meso*-dimethyl imidazolyl porphyrins are among the most active photosensitizers for photoinactivation of multidrug resistant bacteria and biofilms [4]. To fulfil the goal of their clinical translation, a big step in the development of appropriate and scalable synthetic methods is still a challenge.

In this work we present optimization studies for the multigram synthesis of di-imidazolyl porphyrins with yields up to 17%. Their cationic derivatives and selected corresponding reduced chlorin synthesis (Figure 1) will also be discussed. We also discuss the studies of their antimicrobial photodynamic inactivation activity against SARS-CoV-2 and *Escherichia coli* ATCC25922, where promising results were achieved.

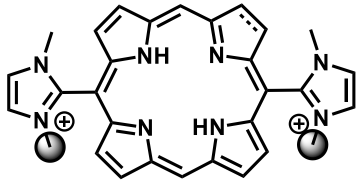

Figure 4: Di-imidazolyl porphyrin derivatives.

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Improving benzisothiazolinone (BIT) effectiveness by cyclodextrin's encapsulation: Ecotoxicity and Antibacterial studies

Alexandra Gaspar[1*], Vânia Silva [2], Aurora Silva [3,4], E. Manuela Garrido[5], Fernanda Borges[1], Jorge Garrido[5]

[1] CIQUP-IMS, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
[2] CIETI/ISEP, Centre of Innovation on Engineering and Industrial Technology/IPP-ISEP, School of Engineering, Porto, Portugal.
[3] Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain.
[4] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal.
[5] CIQUP-IMS, Department of Chemical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Rua Dr. Bernardino de Almeida 431, 4249-015 Porto, Portugal
alexandra.gaspar@fc.up.pt

Isothiazolinones are a group of well-known biocides used as additives in a wide range of industrial products. Among them, benzisothiazolinone (BIT) is widely used in non-cosmetic products, such as industrial chemical products, household detergents, and water-based paint. This biocide is well-known for its potent bactericide, fungicide and algicide properties [1]. However, BIT possesses low water solubility, poor bioavailability, and an inherent sensitization potential, limiting its application. An effective approach to overcoming these constraints is encapsulating the biocide into cyclodextrins. These oligosaccharides are non-toxic and widely used to improve physicochemical properties and/or minimize the deleterious side effects of bioactive compounds. In addition, data found in the literature suggest that combining cyclodextrins with biocides can enhance biocidal activity and minimize environmental pollution [2].

The work herein reported comprises the preparation and characterization of inclusion complexes formed by BIT with cyclodextrins, along with the evaluation of the complexation's effect on the aqueous solubility, antimicrobial activity and ecotoxicity. Overall, it is aimed to provide a useful approach for the industrial production of BIT biocide formulations with improved performance.

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Peptide/ionic liquid-based therapeutics for the topical treatment of skin infections

Ana Gomes[1,*], Lucinda Bessa[2], Iva Fernandes[1], Luisa Aguiar[1,3], Ricardo Ferraz[1,4], Cláudia Monteiro[5,6], Cristina Martins[5,6,7], Nuno Mateus[1],
Paula Gameiro[1], Cátia Teixeira[1,3], Paula Gomes[1]

[1] LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal
[2] current affiliation: CIIEM, Egas Moniz - Cooperativa de Ensino Superior, Almada, Portugal
[3] current affiliation: Gyros Protein Technologies, Tucson, AZ 85714, United States of America
[4] CQBM, Escola Superior de Saúde, Politécnico do Porto, Portugal
[5] i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Portugal
[6] INEB - Instituto de Engenharia Biomédica, Porto, Portugal
[7] ICBAS - Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Portugal
**agomes@fc.up.pt*

Complex wounds, like diabetic foot ulcers or infected burns, are amongst the most complicated skin infections that are associated with polymicrobial biofilms difficult to eliminate. Their treatment often requires an initial debridement and wide-spectrum antibiotic therapy; however, this treatment is at risk given the increasing prevalence of multidrug-resistant (MDR) bacteria that make available antibiotics virtually useless. Therefore, new antimicrobial strategies that efficiently eradicate MDR infections are urgently needed. In the case of severe skin infections, a fast wound-healing process is further required, and recent biomedical approaches have been using collagen-based scaffolds to meet this goal.[1,2] These scaffolds are mostly of animal origin, and to avoid that requires employment of synthetic collagen surrogates, which are difficult to produce.

In view of the above, we advance an alternative approach whereby peptide-ionic liquid conjugates are proposed as potential active pharmaceutical ingredients for topical formulations to tackle skin infections. Such conjugates were anticipated to concomitantly display antimicrobial and anti-biofilm action along with fast healing through, e.g., neocollagenesis-inducing effects. Promising results were obtained with chimeric peptides[3] combining a host-defense sequence[4] with a collagenesis-inducing peptide widely used in cosmetics.[5] Replacing the host defense peptide, in the chimera construct, by an antimicrobial ionic liquid, resulted in a short and potent peptide-ionic liquid conjugate with: i) antibacterial activity, even against MDR clinical isolates of relevant bacterial species, ii) antifungal activity, and iii) collagen-inducing effects on human dermal fibroblasts.[6] This innovative approach where an ionic liquid is covalently linked to a collagen-inducing peptide is therefore a valuable and quite promising strategy for the development of new topical treatments of severe skin infections.

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Guiera senegalensis: On the track of biofungicides development

Rute Moreira[1,*], Federico Ferreres[2], Ángel Gil-Izquierdo[3], Nelson G. M. Gomes[1], Luísa Araújo[4], Eugénia Pinto[5], Romeu A. Videira[1], Paula B. Andrade[1]

[1]REQUIMTE/LAQV, Laboratory of Pharmacognosy, Chemistry Department, Faculty of Pharmacy, University of Porto, Portugal
[2]Department of Food Technology and Nutrition, Molecular Recognition and Encapsulation (REM) Group, Universidad Católica de Murcia, Spain
[3]Research Group on Quality, Safety and Bioactivity of Plant Foods, Department of Food Science and Technology, CEBAS (CSIC), Spain
[4]MDS – Medicamentos e Diagnósticos em Saúde, Guinea-Bissau
[5]Laboratory of Microbiology, Biological Sciences Department, Faculty of Pharmacy, University of Porto, Portugal and CIIMAR/CIMAR–Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Portugal
**rutemartinsmoreira@hotmail.com*

The pest resistance against available synthetic fungicides is a widespread and increasing problem, with impact on crop production and public health. Thus, biofungicides development is a challenge to fungal pest control. Herein, the methanol leaves extract of *Guiera senegalensis* J. F. Gmel., a medicinal shrub distributed in semi-desert areas of Africa [1], was characterized regarding its chemical composition and antifungal activity. Bioassay guided fractionation of the extract was used to connect the chemical composition with the bioactivity. HPLC-DAD-ESI(Ion Trap)-MS^n and UPLC-ESI-QTOF-MS^2 analyses revealed a complex mixture of compounds, containing, at least, 34 phenolic compounds and 14 porphyrin-containing molecules. While the phenolic profile is dominated by flavonol 3-*O*-glycosylated derivatives (19), galloyl derivatives (10) and a naphthyl butenone guieranone, the porphyrin-containing compounds include the chlorophylls *a* and *b* and their catabolites resulting from oxidation before and after the loss of phytol group. The methanol extract was fractionated under a silica gel solid phase procedure to obtain a lipophilic fraction enriched in guieranone, chlorophyll derivatives and membrane lipids, collected with ethyl acetate, and a phenolic-enriched fraction, collected with methanol, as unveiled by HPLC-MS/MS analysis.

Assays with the filamentous fungi *Aspergillus fumigatus*, *Fusarium oxysporum* and *Colletotrichum gloeosporioides* revealed limited antifungal activity for the crude extract and the phenolic-enriched fraction. However, the lipophilic fraction showed antifungal activity against the three filamentous fungi species with minimum inhibitory concentrations (MIC) ranging from 500 to 2000 µg/mL. The effects against yeasts (*Saccharomyces cerevisiae*, *Candida albicans*, *Candida krusei* and *Cryptococcus neoformans*) are worth to highlight, with MICs values ranging from 8 to 250 µg/mL, confirming the antifungal activity of the lipophilic fraction from *G. senegalensis* leaf methanol extract. The mechanisms of action are still under investigation, but effects on mitochondria with selective inhibition of complex II were already detected.

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Unveiling membrane dependent mechanism of action of molecules with anticancer activity

Daniela Oliveira[1*], **Filipa A. Soares**[1,2], **Salette Reis**[1], **Cláudia Nunes**[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313, Porto, Portugal
[2]ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Porto, Portugal
**dans.oliveira22@gmail.com*

Due to potential synergistic or addictive effects, the combination of conventional anticancer drugs with bioactive compounds has been investigated to create new and less toxic therapies. Tamoxifen (TAM) is a drug typically used in hormonal therapy for the treatment of estrogen receptor (ER) positive breast cancer (BC) and epigallocatechin-3-gallate (EGCG) is the predominant polyphenol present in green tea, widely known for its anticancer activity. Although their anti-tumor effects are well described, their real mode of action is not completely understood. Additionally, evidence suggests that both molecules can interact with the plasma membrane, and therefore this structure can be involved in their alternative mechanisms of action [1,2]. Thus, the aim of this work was to study the anticancer activity of EGCG and TAM alone and in combination in different BC cell lines, underlying their molecular mechanisms concerning the cell membrane.

Firstly, the cellular viability of ER-positive (+) MCF-7 and ER-negative (-) MDA-MB-231 BC cells were assessed by the resazurin assay, after 48 h incubation with EGCG and TAM alone and combined. L929 fibroblasts were also used as a reference line to study the side effects in non-cancer cells. EGCG alone was cytotoxic at high concentrations, with its maximum inhibitory effect at 600 µM. Additionally, TAM proved to be more effective in ER (+) cells. From the combinatorial studies, no beneficial effects were obtained by the combination of EGCG and TAM in MCF-7 cells. Contrarily, some combinations of EGCG and TAM produced synergistic effects in MDA-MB-231.

Then, the molecular interactions of EGCG and TAM with lipid cell membranes were investigated. For this purpose, Langmuir monolayers composed of 1,2-dipalmitoyl-*sn*-glycero-3-phospho-L-serine (DPPS), 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), sphingomyelin (SM), and cholesterol (Chol) were assembled either alone or in combinations to mimic different lipid domains. Two biophysical techniques were used, namely, Langmuir isotherms and Brewster angle microscopy (BAM), to access the influence of anticancer molecules on lipid monolayers properties and morphology, respectively. EGCG showed to have a strong affinity to DPPC, causing the fluidization of PC monolayers. Since PCs are the major phospholipids in natural cell membranes, the EGCG-PCs interactions might be the explanation of the pleiotropic effects and anticancer activity of this compound. TAM caused the condensation of the monolayers. Therefore, its mechanism of action can be related to the decrease of cancer cell division. Additionally, this drug interacts preferentially with anionic DPPS, which is exposed in the extracellular leaflet of cancer cell membranes.

The results obtained in this work with the information present in the literature showed that EGCG and TAM alone or combined can interact with lipid rafts increasing the membrane fluidity of these regions. Consequently, alteration in the location or activity of transmembrane proteins that upregulate signal pathways involved in cancer cell growth and proliferation may occur. Therefore, important oncogenic proteins are less expressed decreasing the cell viability of MDA-MB-231. Although interesting conclusions were obtained additional studies and methods should be carried out to draw a more complete scenario of the interactions and biological effects of both molecules in membranes.

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QS31

Water-soluble pyridinium-pyrazole phthalocyanines for photodynamic inactivation of Phage Phi6 as SARS-CoV-2 Model

Sara R.D. Gamelas[1,*], Thierry J. Gomes[2], Maria Bartolomeu[2], M. Amparo F. Faustino[2], João P.C. Tomé[3], Augusto C. Tomé[1], Adelaide Almeida[2], Ana T.P.C. Gomes[2], Leandro M.O. Lourenço[1]

[1]LAQV-REQUIMTE and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]CESAM and Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal.
[3]CQE, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049–001, Lisboa, Portugal.
**sara.gamelas@ua.pt*

The severe acute respiratory syndrome coronavirus (SARS-CoV-2) is the leading cause of the COVID-19 pandemic and is transmitted by virus laden respiratory, water droplets or contaminated surfaces. However, its presence in water bodies might be responsible for virus persistence and propagation to the human population. A significant amount of the wastewater released into the environment is not properly treated to efficiently eliminate microorganisms as e.g., viruses [1]. Photodynamic inactivation (PDI) of microorganisms has already shown to be effective against bacteria, fungi, and viruses [2-4]. During this treatment process, the short-lived excited state of the PS is converted into a long-lived triplet state that allows obtaining the reactive oxygen species (ROS), such as $^1O_2$, which lead to severe oxidation of the vital cellular constituents of the microbial targets [4]. This study evaluated the use of quaternized zinc(II) phthalocyanines (ZnPcs) **2a** and **3a** for the PDI hypothesis to be considered a suitable approach for the inactivation of Phage ϕ6 as a surrogate for SARS-CoV-2 in wastewater treatment [5]. Thus, two new octa-substituted ZnPcs (**2a** and **3a**, Fig. 1), bearing pyrazole-pyridinium groups, were synthetized and characterized. The PDI assays were performed with the quaternized ZnPcs **2a** and **3a** at low concentrations under white light irradiation with two irradiance intensities (50 and 150 mW.cm^{-2}). For the PDI assays, the Phage ϕ6 was used as a surrogate for SARS-CoV-2.

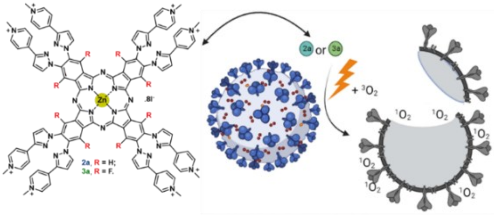

Fig.1. Inactivation of phage ϕ6 using cationic ZnPcs **2a** and **3a**.

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β-Phospholactams as a novel chemical tool to target serine hydrolases

Rita Félix[1*], **Carlos A. M. Afonso[1]**, **Rui Moreira[1]**

[1]Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia da Universidade de Lisboa,
Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal;
**ritafelix@ff.ulisboa.pt*

Serine hydrolases represent nearly 1% of all proteins in mammalian cells [1], playing vital roles, such as promoting tumorigenesis and inflammation. Moreover, serine hydrolases are also involved in relevant pathologies such as cancer. In particular, Human Neutrophil Elastase (HNE), a serine hydrolase expressed in polymorphonuclear neutrophils, is present in the tumor microenvironment and recent studies showed that it promotes tumor proliferation and metastasis [2], making it important to build tools for a proper understanding of the potential of this enzyme in cancer treatment.

In recent studies, four-membered rings have been used to target serine hydrolases and at this point, the structural requirements for acylation and sulfonylation [3] of catalytic amino acids by four-membered ring probes are established. However, phosphonylation remains largely unexplored.

The present work reports the synthesis of probes bearing as warhead a phospholactam ring (Fig. 1). These type of compounds are expected to promote phosphonylation of the catalytic serine residue of HNE. However, phospholactams remain a synthetic challenge.

This work started with the synthesis of diazo phosphoamidate **1**. The cyclization step to obtain the *β*-phospholactam ring (Fig. 2) was optimized to find the best conditions, to this optimization the HPLC method was developed to follow the reaction. Therefore, we will synthesize probes with this warhead, and a preliminary study of the reactivity of this type of compounds will be performed to understand if phopholactams can become an important tool to analyze serine hydrolases, mainly HNE. We also want to obtain a crystallographic structure of the novel probes with HNE or PPE.

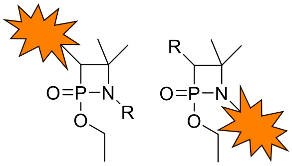
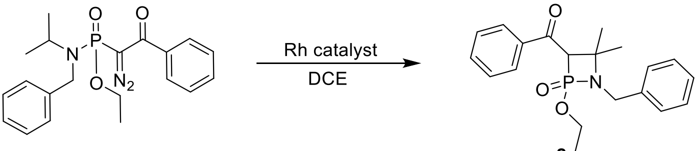


Fig. 2. *β*-phospholactam-based ABPs.



1

2

Fig. 3 Cyclization reaction optimized to obtain *β*-phospholactam **2**.

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Synthesis, characterization and antibacterial profile of new GUMBOS

Fábio M. S. Costa[1,*], Rocío L. Pérez[2,3], Isiah M. Warner[2,4], Marieta L. C. Passos[1], M. Lúcia M. F. S. Saraiva[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, 4050-313, Porto, Portugal
[2]Department of Chemistry, Louisiana State University, 70803, Baton Rouge - LA, United States
[3]Department of Chemistry and Biochemistry, Georgia Southern University, 30461, Statesboro, GA, US
[4]Department of Chemistry, Cincinnati University, 45221, Cincinnati, OH, United States
*up201206985@up.pt

Antimicrobial resistance (AMR) has become a global health and development threat. It has been a challenge for the medical and pharmaceutical fields in the last decades with increasing numbers of emerging antibiotic-resistant infections and subsequent deaths. Global initiatives to deliver new stand-alone or complementing alternative therapies are urgently needed [1]. Ionic liquids (ILs) and a group of uniform materials based on organic salts (GUMBOS) [2] have been recently explored as an adjuvant therapy [3]. Using active pharmaceutical ingredients (APIs), such as antibacterials or antiseptics, and modifying their structures to modulate and increase their pharmacological activity is a pathway to create agents with novel properties. The main objective of this work is the synthesis, physicochemical characterization and antimicrobial profile evaluation of new fluoroquinolone-based GUMBOS.

Ciprofloxacin [Cip]-based GUMBOS were prepared using a simple anion metathesis reaction, where the chloride [Cl^-] anion was exchanged using three bulky anions (bis(perfluoroethylsulfonyl)imide [BETI], tetraphenylborate [TPB], and deoxycholate [Dxc]). GUMBOS formation was confirmed by structural characterization using NMR and FTIR spectroscopy as well as HRMS. Thermal stability was investigated using TGA and DSC. Thermal decomposition (T_{start}) started between 211-279°C and the onset temperatures (T_{onset}) ranged from 275-303°C, except for the parental [HCl] form and the [TPB] compounds which were all lower. Octanol/water partition coefficient ($K_{O/W}$) values were determined, with the majority of GUMBOS being more hydrophilic than lipophilic. The *in vitro* antimicrobial study was carried out using the broth microdilution assay with *S. aureus* and *E. coli*. Antibacterial results (Figure 1) showed that GUMBOS at 0.25 mg L^{-1} inhibited bacterial growth, with greater significance for the positive controls against *S. aureus* (Fig. 1a). Increasing GUMBOS concentration to 25 mg L^{-1}, a higher antibacterial activity was detected for both bacterial strains, with lower bacterial growth towards *E. coli* (Fig. 1b). Overall, complexation with [Dxc] was the least effective antibacterial form of GUMBOS, and the majority of GUMBOS presented similar activities as the positive controls. Thus, these new compounds have potential to be further investigated and be used to help in the fight against the antimicrobial resistance growing threat.

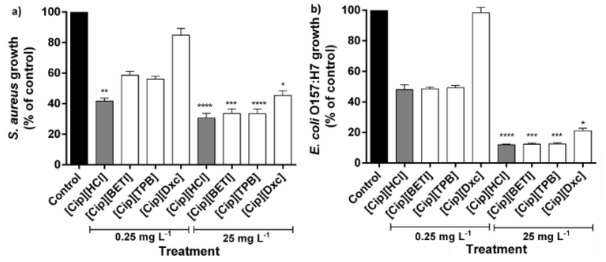

Fig.1. Antibacterial activity after 24h exposure to GUMBOS on *S. aureus* and *E. coli*.

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Tricyclic compounds derivatives as new potential neuroprotective agents

Márcia S. Martins[1,2*], Miguel Maia[1,2], Eva Gil-Martins[3], Luís Gales[4,5], Fernando Remião[3], Madalena M. M. Pinto[1,2], Renata Silva[3*], Emília Sousa[1,2*]

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2]CIIMAR–Interdisciplinary Centre of Marine and Environmental Research, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal
[3]UCIBIO – REQUIMTE, Department of Biological Sciences, Laboratory of Toxicology, Faculty of Pharmacy of the University of Porto, 4050-313 Porto, Portugal
[4]Institute for Innovation and Health Research (i3S), 4200-135 Porto, Portugal
[5]Department of Molecular Biology, Biomedical Sciences Institute (ICBAS), University of Porto, 4050-313 Porto, Portugal
** rsilva@ff.up.pt (R.S.); esousa@ff.up.pt (E.S.)*

The focus on the strategy of "one molecule, multiple targets" is becoming one of the most interesting approaches for the development of an efficacious Alzheimer's disease (AD) treatment given the multifactorial character of this neurological pathology. Hence, the development of a multitarget-direct ligand capable of inhibit β-secretase (BACE-1) and glycogen synthase kinase 3 (GSK-3β), two enzymes involved in the formation of amyloid plaques and neurofibrillary tangles, respectively, would be beneficial once it will act in two hallmarks of AD [1,2]. The main goal of this work was the synthesis of potential dual BACE-1/GSK-3β inhibitors and the evaluation of their neuroprotective properties *in vitro*.

Ten compounds were successfully synthetized, by conjugation of tricyclic scaffolds with aliphatic amines, through amides, after reducing to the corresponding amines, with yields between 18 % and 95 %. The structure characterization was performed by spectroscopic methods, such as nuclear magnetic resonance, infrared spectroscopy, and X-ray crystallography. Their neuroprotective properties were evaluated using differentiated SH-SY5Y cells and several compounds demonstrated the possibility of potential protect the cells against the cytotoxicity induced by three chemical aggressors, MPP^+, iron (III), and β-amyloid (Aβ) peptide, as well as potential to activate P-glycoprotein (P-gp). The compounds with halogen atoms in their structures demonstrated a higher protection against iron (III)-induced cytotoxicity, which was not dependent on iron chelation. Neuroprotective effects against $A\beta_{1-42}$-induced cytotoxicity were shown to be dependent on P-gp activation.

In conclusion, a small library of tricyclic derivatives was successfully obtained and characterized by the neuroprotective properties of several compounds with potential for treatment of neurodegenerative diseases.

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QS35

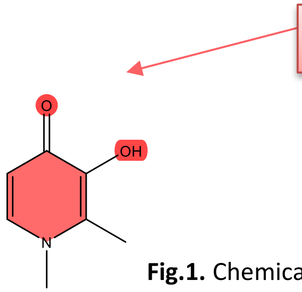
DEVELOPMENT OF NEW MULTITARGET-DIRECTED LIGANDS WITH POTENTIAL APPLICATION IN ALZHEIMER'S DISEASE

Carla Lima[1], Fernanda Borges[1], Sofia Benfeito[1*]

[1]CIQUP-IMS- Centro de Investigação em Química, Instituto Ciências Moleculares
Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Porto, Portugal;
** ester.benfeito@up.pt*

Alzheimer disease (AD) is the most common neurodegenerative disease featuring progressive and degenerative neurological impairments resulting in memory loss and cognitive decline. Nowadays the existing pharmacological therapies involves the use of acetylcholinesterase (AChE) inhibitors (donepezil, rivastigmine, galantamine), which is only a palliative treatment and does not modify the course of the disease. One of the pathologies associated with AD involves the intracellular production of reactive oxygen species by the mitochondria, thus leading to oxidative stress, disruption of metal homeostasis, such as iron and cholinergic deficit. In this context, find new safe and efficient drugs for AD are urgently needed. In this work, and following a multitarget strategy, it is hypothesized that tackling iron-induced cell death (ferroptosis) while inhibiting the cholinesterases (AChE and BChE) might have therapeutic impact for AD patients. With this in mind, we aim to design and develop smart bifunctional compounds, that combine in a single molecule a short-term symptomatic approach (cholinergic therapy via AChE and butyrylcholinesterase (BChE) inhibition) with a long-term disease-modifying intervention (modulation of ferroptosis via iron chelation).

Deferiprone (DFP) is an iron chelator used in treatment of thalassemia and, due to its low molecular weight, favorable hydrophobicity and neutral charge, it becomes a privileged structure in drug discovery programs. In this way, a new library of 18 compounds based on DFP was synthesized aiming to act on oxidative stress and acetyl/butyrylcholinesterases, maintaining the iron chelating capacity of its precursor. Structural characterization of the newly synthesized compounds was carried out by NMR (^{1}H, ^{13}C and DEPT) spectroscopy. Then, several in vitro ADMET properties were evaluated. Biological screening has included the assessment of acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) inhibitory activities, in vitro iron chelation activity and in vitro blood-brain barrier (BBB) penetration ability. The results obtained so far will be presented in this communication.



Chelates Fe(III): inhibits **ferroptosis**

Fig.1. Chemical structure of deferiprone.

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Following-up bladder cancer patient's response to therapy

Luís B. Carvalho[1,2,*], J. L. Capelo[1,2], Carlos Lodeiro[1,2], Luis Campos Pinheiro[3,4], Mariana Medeiros[4,5] & Hugo M. Santos[1,2,5,]**

[1]BIOSCOPE Research Group, LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade NOVA de Lisboa 2829-516, Caparica, Portugal.
[2]PROTEOMASS Scientific Society, Madan Parque, Rua dos Inventores, 2825-182 Caparica, Portugal.
[3]NOVA Medical School. NOVA University of Lisbon, Lisbon, Portugal.
[4]Urology Department, Central Lisbon Hospital Center, Lisbon, Portugal.
[5]Department of Pathology, University of Pittsburgh Medical Center, Pittsburgh, PA, United States.
[*] lab.carvalho@campus.fct.unl.pt
[**] hmsantos@fct.unl.pt

Bladder cancer is one of the most common cancers, with over half a million new cases recorded in 2020 worldwide [1]. Among the different subtypes of BC, T1 stage patients have a high risk of progression and recurrence, requiring constant surveillance by an invasive endoscopy of the bladder via the urethra. As a result of ongoing monitoring, BC is one of the most debilitating and expensive cancer to treat per patient.

There is currently no one-size-fits-all method for improving bladder cancer treatment and monitoring [2,3]. To close this gap, we developed the differential Personal Pathway index (dPPi), a simple, cost-effective, non-invasive, and personalized patient monitoring tool. dPPi harnesses the potential of high-resolution mass spectrometry by integrating proteomic data from urine samples onto biological pathways that represent each person's health condition.

To validate this approach, the urinary proteomes of 30 individuals pathologically diagnosed with clear T1 stage BC were analysed. As proof of concept, the dPPi algorithm was also used to track the proteome changes of six patients in a personalized way during the course of disease and therapy.

Our findings demonstrate that by including the urine proteome and biochemical pathway analysis into the dPPi approach enables BC course monitoring. Furthermore, this unique approach track down patients and, when paired with clinic data, help in clinical decision-making, ultimately achieving the goal of prescriptomics [4].

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High-resolution absolute quantitative proteomics revealed new immunohistochemical markers of oncocytic renal neoplasms

Hugo M. Santos[1,2,3]*, William LaFramboise[3], Swati Satturwar[3], Dimitrios Korentzelos[3], Sheldon Bastacky[3], Gabriela Quiroga-Garza[3], Rajiv Dhir[3], Jacek R. Wiśniewski[4], Carlos Lodeiro[1,2] and José L. Capelo[1,2]

[1] BIOSCOPE Group, LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
[2] PROTEOMASS Scientific Society, Madan Park, 2829-516 Caparica, Portugal.
[3] Department of Pathology, University of Pittsburgh Medical Center, Pittsburgh, PA, USA.
[4] Biochemical Proteomics Group, Department of Proteomics and Signal Transduction, Max-Planck-Institute of Biochemistry, Martinsried, Germany.
* *hmsantos@fct.unl.pt*

Oncocytic renal neoplasms are characterized by overlapping histologic, immunohistochemical, and molecular features that challenge accurate diagnosis [1]. The subset of renal oncocytic neoplasms includes benign renal oncocytoma and malignant chromophobe renal cell carcinoma [1, 2]. Our proteome-wide absolute quantitative analysis demonstrates uncovered new immunohistochemical markers for the accurate diagnosis of oncocytic renal neoplasms diagnosis. MS-data was validated using semi-quantitative immunohistochemistry with 128 samples assessed on tissue micro-aways. Our approach has identified and validated LAMP1 and HK1 as efficient markers of chromophobe renal cell carcinoma and renal oncocytoma, respectively [2].

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The effect of varying the complexity of amines introduced into the squaric ring on the photobiological activity of aminosquaraine dyes

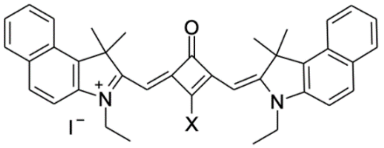
Eurico Lima[1,2*], **Andreia Barroso**[1], **Octávio Ferreira**[2], **Renato Boto**[2], **José R. Fernandes**[1], **Paulo Almeida**[2], **Samuel M. Silvestre**[2,3], **Adriana O. Santos**[2], **Lucinda V. Reis**[1]

[1]Chemistry Centre of Vila Real (CQVR), University of Tras-os-Montes and Alto Douro,
Quinta de Prados 5001-801, Vila Real, Portugal
[2]Health Sciences Research Centre (CICS-UBI), University of Beira Interior,
Av. Infante D. Henrique 6201-506, Covilhã, Portugal
[3]Centre for Neuroscience and Cell Biology (CNC), University of Coimbra,
Rua Larga 3000-517, Coimbra, Portugal
eurico_lima@icloud.com

Despite being known to be more cytotoxic under non-irradiated conditions than the four-membered central ring unsubstituted squaraine dyes, aminosquaraine dyes address some of their shortcomings, such as their improved solubility in aqueous media. Given this advantage, and the fact that they absorb quite efficiently at even higher wavelengths, several researchers have focused on studying aminosquaraines as possible photosensitizers for photodynamic therapy. By varying the heterocyclic units from which they are derived, as well as the number of carbons of the *N*-alkyl chains, very significant *in vitro* biological effects can be observed in their photodynamic activity. More recently, indolenine derivatives have shown high phototherapeutic promise; however, due to their complex purification, few aminosquaraines have been evaluated.

Analogous to indolenine derivatives, this communication presents the synthesis of six *N*-ethyl benz[*e*]indole aminosquaraine dyes (Fig. 1) and their *in vitro* study as potential photosensitizers for photodynamic therapy. Initially, all dyes were evaluated for their cytotoxicity in the dark and under irradiation conditions using the MTT assay in five cell lines (NHDF, Caco-2, HeLa, MCF-7 and PC-3). A self-made light-emitting diode system centered at 700 nm was used for irradiation. Complementary studies to determine their cellular localization, and asssess their genotoxicity, mechanism of death and cell cycle arrest were approached for the aminosquaraines with more significant biological promise.

All aminosquaraines showed interesting biological activity since lower half-maximal inhibitory concentration values for irradiated conditions were obtained compared to non-irradiated treatments. Dyes **1** and **4** were selected for further studies. These dyes were found to be preferentially located in the mitochondria and may be contained in organelles other than lysosomes. Significant genetic damage was observed even under non-irradiated conditions. Apoptosis is suggested as the mechanism by which cells die after light activation of the potential photosensitizers, and a slight increase in cells in the G2/M phase was observed compared to untreated events.



1: X = NH_2
2: X = $NHCH_3$
3: X = $N(CH_3)_2$
4: X = $NHCH_2CH_2OH$
5: X = $N(CH_3)CH_2CH_2OH$
6: X = $N(CH_2CH_2OH)_2$

Fig.1. Structural formula of aminosquaraine dyes **1**-**6**.

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Anti-proliferative effect of novel chlorophyll derivatives in breast cancer cell lines

Cristina J. Dias[1,2,*], Luisa Helguero[2], M. Amparo F. Faustino[1]

[1]LAQV-Requimte and Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal
[2]iBiMED - Institute of Biomedicine, Department of Medical Sciences, University of Aveiro, 3810-193 Aveiro, Portugal
**cristina.jesus.dias@ua.pt*

Breast Cancer (BC) has the highest incidence (24.5%) and mortality rate (15.5%) among women worldwide [1]. It is estimated that the total number of women affected by BC will increase by 50% in 2040 [2]. BC is an heterogeneous disease of which 5-10% diagnoses are of the triple-negative subtype, for which no satisfactory therapy exists. Moreover, luminal subtype can be treated with hormonal therapy, but about 1/3 of the patients develop resistance and relapse [3]. Therefore, it is crucial to find safe and innovative strategies to bring a better prognosis to the patients.

The interest in localized treatments, with minimal side effects, led to breast cancer therapies based on the application of photoactive molecules [3]. Photodynamic Therapy (PDT), a localized treatment modality, combines dioxygen, visible light and a photoactive molecule – photosensitizer (PS); this PS when excited by light can produce reactive oxygen species (ROS), such as singlet oxygen – an highly reactive specie, capable of triggering cell death [3,4].

The selection of the photoactive molecule depends on its specific application, but when it's about cancer, molecules that strongly absorb in the therapeutic window (650 – 800 nm), such as chlorin and chlorophyll derivatives, are of particular interest, taking advantage of better tissue penetration of light in the red region of electromagnetic spectrum [3,4].

The photodynamic activity of different chlorophyll derivatives was evaluated using crystal violet assay, in metastatic and non-metastatic BC cell lines. The photodynamic efficacy of the different derivatives and their potential for therapy will be discussed.

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Ministério da Ciência, Tecnologia e Ensino Superior) of LAQV-REQUIMTE through the projects UIDB/50006/2020 and UIDP/50006/2020, and of Institute for Biomedicine—iBiMED through the projects UIDB/04501/2020, UIDP/04501/2020 and MEDISIS (CENTRO-01-0246-FEDER-000018). The authors thank the University of Aveiro and the Portuguese NMR Network. Cristina J. Dias thanks FCT/MCTES for her PhD grant (SFRH/BD/150676/2020).

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The wound healing properties of starch-based photoactive materials

A. Sofia M. Joaquinito[1*], Paulo Brites[1], Carlos J. P. Monteiro[1], Nuno M. M. Moura[1], Marta Martínez Sanz[2], M. Amparo López Rubio[2], Idalina Gonçalves[3], Paula Ferreira[3], M. Graça P. M. S. Neves[1], Susana G. Guerreiro[4,5], M. Amparo F. Faustino[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Food Safety and Preservation Department, IATA-CSIC, Avda. Agustín Escardino 7, 46980, Paterna, Valencia, Spain
[3]CICECO, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193, Aveiro, Portugal
[4]I3S, Instituto de Investigação e Inovação em Saúde, 4200-135 Porto, Portugal
[5]Department of Biomedicine, Biochemistry Unit, Faculty of Medicine University of Porto, 4200-319 Porto, Portugal
a.joaquinito@ua.pt

In the last decades, the contribution of biotechnology on science, namely under the context of biomedical applications is having an extraordinary impact. However, in this scenery, chronic wounds, still present a challenge to treat, having no consensual, effective, and easy treatment plan [1]. Photodynamic therapy (PDT) and light therapies have been gaining focus over the last few decades, not only as a well-established cancer treatment, but also as alternative approaches for localized antimicrobial treatments. More recently, although the scope of these therapies has been expanded for wound healing [2], is still an underexplored research area. When envisioning a wound healing application, a solid material supporting a photosensitizer might be the best choice for the delivery. Starch can be used to prepare biocompatible thermoplastic materials and the possibility of using it as a support for PS agents was considered.

In this work, the effect of starch-based photoactive materials containing 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin or 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin on ROS formation and cellular viability, migration and adhesion of Human Microvascular Endothelial Cells (HMEC) and Human Dermal Fibroblasts (HDF), two different cell types involved on the dermal healing process [3] was studied.

Acknowledgements

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Design, synthesis and evaluation of novel antileishmanial agents

Carlos F. M. Silva[1], **Teresa Leão**[2,3], **Filipa Dias**[2,3], **Ana M. Tomás**[2,3], **Diana C. G. A. Pinto**[1], **Pedro A. Fernandes**[4], **Artur M. S. Silva**[1]

[1]LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal; [2]i3S, Instituto de Investigação e Inovação em Saúde, Porto, Portugal; [3]ICBAS, School of Medicine and Biomedical Sciences, Universidade do Porto, Porto, Portugal; [4]UCIBIO, REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade Do Porto, Porto, Portugal.
silva.c@ua.pt

Leishmaniasis is one of the most neglected diseases in modern times, affecting mainly people from developing countries of the tropics, subtropics, and the Mediterranean basin, with approximately 350 million people considered at risk of developing this disease. [1] The incidence of human leishmaniasis has increased over the past decades due to failing preventing and therapeutic measures - there are no vaccines and chemotherapy is problematic.[2] Acridine derivatives constitute an interesting group of nitrogen-containing heterocyclic compounds, with several derivatives being associated with numerous bioactivities.[3] In particular, there are reports on acridine derivatives exhibiting interesting antileishmanial activity, including derivatives with a vast variety of substituents, or even bis- and tetra-acridine complexes.[4] The present work builds on theoretical studies focusing on a specific enzyme of the parasite, *S*-adenosylmethionine decarboxylase (AdoMet DC), nitrogen-containing heterocycles emerged as potential inhibitors, evidencing these scaffolds as promising building block for novel antileishmanial pharmaceuticals. Thus, several derivatives from both groups of compounds (**1** and **2**) have been synthesized, their activity against *Leishmania infantum* promastigotes evaluated, and a structure-activity relationship (SAR) study was developed based on the results obtained (Figure 1). Finally, these two types of compounds were also evaluated towards their toxicity against macrophages. The results demonstrated that numerous derivatives from both groups present promising antileishmanial properties, depending on the carbon chain length between fragments (group 1) and on the nucleophile introduced in each position of the cyanuric chloride scaffold (group 2) In conclusion, four compounds, one from group **1** and three from group **2**, present IC_{50} values below 1.0 µM, in association with low levels of toxicity, leading to an interesting starting point for the development of novel antileishmanial treatments.

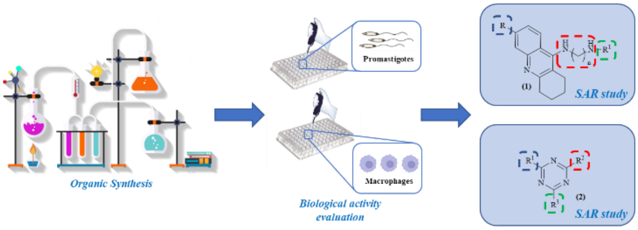

Figure.1. Synthesis and biological evaluation of 1,2,3,4-tetrahydroacridines (**1**) and 1,3,5-triazines (**2**) against *Leishmania.*

Acknowledgements
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Synthesis and biological evaluation of acridine-triazine hybrids as acetylcholinesterase and butyrylcholinesterase inhibitors

Ana P. D. de M. S. Guerrinha[1], Carlos F. M. Silva[1], Diana C. G. A. Pinto[1], Artur M. S. Silva[1]

[1]LAQV-REQUIMTE& Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal
patriciaguerrinha@ua.pt

Alzheimer’s disease (AD) is one of the most prevalent progressive and multifactorial neurodegenerative disorders, often associated with dementia, for which there are no definitive treatments or prophylactic agents.[1] This disease affects mainly older people, affecting up to 20% of individuals over 80 years old and constituting one of the leading causes of death in this age group, causing loss of memory and cognitive capacities through mental deterioration.[2] Acridine derivatives are versatile nitrogen-containing heterocyclic compounds often described as great drug candidates and an ideal starting point for designing novel multitarget compounds.[3] In particular, several acridine derivatives have been described with promising features regarding AD due to their ability to inhibit acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE).[4] In turn, triazines are also nitrogen-containing heterocyclic compounds with a wide array of described biological activities.[5] 1,3,5-Triazines are described as promising drug candidates for AD by their neuroprotective properties allied with their AChE and β-secretase-1 (BACE-1) inhibitory effects.[6] Focusing on the inhibitory activity of AChE and BuChE enzymes, several derivatives (**5**) containing both the acridine (**1**) and triazine (**4**) scaffolds were synthesized, and their inhibitory activities were evaluated (Figure 1). The results revealed that various derivatives present promising anti-AChE and anti-BuChE properties, allowing the elaboration of a preliminary structure-activity relationship.

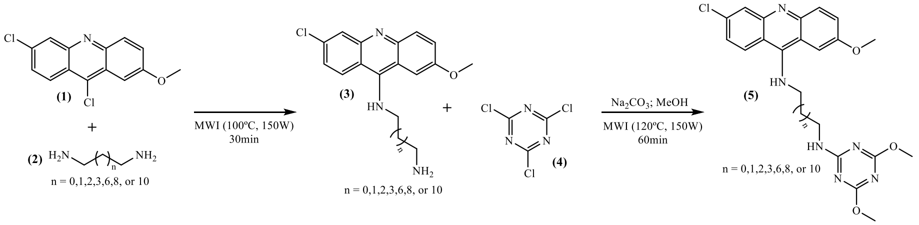

Figure.1. AChE and BuChE inhibitors based on the acridine and triazine scaffolds

Acknowledgements

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Silica nanomaterials based on ionic antimicrobial agents for infectious therapeutic diseases

L. Filipe[1,*], B. de Juan Mora[1], C. Alves[2], M. Ribeiro Carrott[3], T. de Sousa[4], P. Poeta[4], L. C. Branco[1], S. Gago[1]

[1]LAQV REQUIMTE, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa,
Departamento de Química, Campus de Caparica, 2829-516 Caparica, Portugal
[2]MARE—Marine and Environmental Sciences Centre, Politécnico de Leiria, Avenida Porto de Pesca,
2520-630 Peniche, Portugal
[3]LAQV-REQUIMTE, Universidade de Évora, Instituto de Investigação e Formação Avançada,
Departamento de Química e Bioquímica, Escola de Ciências e Tecnologia, Colégio Luís António
Verney, 7000-671 Évora, Portugal
[4]Microbiology and Antibiotic Resistance Team (MicroART), Universidade de Trás-os-Montes e Alto
Douro, Departamento de Ciências Veterinárias, 5000-801 Vila Real, Portugal
**lm.filipe@campus.fct.unl.pt*

Infectious diseases are the second major cause of death worldwide and the antibiotic treatment sometimes fails due to drug resistant strains or to insufficient activity or concentration of antibiotics at the site of infection [1]. Mesoporous silica nanoparticles (MSNs) are very promising nanomaterials to treat bacterial infections when combined with pharmaceutical drugs.

In this communication we report a synthetic method to obtain three different sets of nanomaterials, based on the immobilization of fluoroquinolone antibiotics as counter-ions of cholinium, 3-picolinium and methylimidazolium materials. The present work concerns the synthesis of ionic liquids functionalized with a propyltriethoxysilane moiety, which is then grafted on the surface of the MSN. The corresponding materials undergo an ionic exchange reaction to afford the immobilized antibiotic. Ciprofloxacin and norfloxacin were used in this study, combined with cholinium cation ([MSN-Chol][Cip] and [MSN-Cho][Nor]) as follow-up of a previous finding from our research team [2]. Similarly, 3-picolinium and methylimidazolium cations were combined solely with ciprofloxacin ([MSN-3-Pic][Cip] and [MSN-1-MiM][Cip]) as new materials, yet to be published. Non-supported analogues were also prepared and characterized for comparison.

All materials were characterized by NMR spectroscopy, FT-IR, elemental analysis, X-ray powder diffraction and N_2 adsorption at 77 K. The present method can be extended to engulf a broader range of antibiotics, together with different combinations of ionic liquid precursors, which makes the current protocol a very attractive alternative to the production of novel pharmaceutical ingredients immobilized on nanoparticles. Furthermore, the use of nanoparticles to treat infectious diseases can lead to more active formulations, smaller doses and fewer side effects [2].

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Conjugation of carbon nanomaterials with tetrapyrrolic macrocycles: Applications & challenges

Carla I.M. Santos[1,2*], Laura Rodriguez-Pérez,[3] Gil Gonçalves [4], M. Amparo Faustino[1], M. Angelés Herranz[3], Nazario Martín[3], José M. G. Martinho[2], Ermelinda Maçôas,[2] M. Graça P.M.S. Neves[1]

[1]LAQV-REQUIMTE, Department of Chemistry of University of Aveiro, 3810-193 Aveiro, Portugal
[2]Centro de Química Estrutural, Institute of Molecular Science and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049–001 Lisboa, Portugal
[3] Department of Organic Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, E-28040 Madrid, Spain
[4] TEMA-Nanotechnology Research Group, Mechanical Engineering Department, University of Aveiro, Campus Universitario de Santiago, 3810-193 Aveiro, Portugal
*cims@ua.pt

Photodynamic therapy (PDT) has been considered as a non-invasive treatment with less side effects when compared to conventional cancer treatments such as chemotherapy, radiotherapy and immunotherapy. In this therapeutic approach, the activation of molecules by visible or near infrared light irradiation at an appropriate wavelength in the presence of dioxygen is fundamental to generate cytotoxic reactive oxygen species (ROS), responsible by the oxidation of cellular constituents in the target tissue provoking the cell death. Ideally, the dyes, known as photosensitisers (PS), should be compounds with insignificant dark toxicity and some degree of hydrophilicity.

Among the high number of PS that have been studied in vitro and in vivo a special attention has been dedicated to porphyrins, corroles and phthalocyanines due to their high singlet oxygen yield, low toxicity and unique optical and electronic properties. However, the poor water solubility of tetrapyrrolic macrocycles can lead to formation of aggregates compromising their use in PDT.

To prevent aggregation, several studies have been focused on the incorporation of PS into nanomaterials such as carbon nanomaterials. The development of conjugates based on corroles/porphyrins /phthalocyanines and carbon nanomaterials for cancer therapy is a recent topic of research with promising results found for graphene quantum dots (GQDs).

Graphene quantum dots (GQDs) possess excellent optical and electronic properties coupled with high photostability, aqueous solubility and biocompatibility. The presence of carboxyl and hydroxyl groups on their surface and edges enable covalent attachment, electrostatic interactions and hydrogen bonding with other suitable moieties [1]. In addition, the nonlinear optical response of GQDs presents great opportunities for the development of optical sensors operating in biological media [2].

In the present study GQDs have been conjugated covalently and non-covalently with tetrapyrrolic macrocycles (corroles, porphyrins and phthalocyanines). The optical and structural characterization of the resultant hybrid materials is discussed. Preliminary studies on cellular uptake and distribution, using confocal and multiphoton microscopy, are presented [3-5].

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Porfirinas sulfonamidas como agentes fotossensibilizadores para inativação de bactérias multirresistentes

Sofia Sarabando[1], **Cristina J. Dias**[1], **Cátia Vieira**[2], **Maria G. P. M. S. Neves**[1], **Adelaide Almeida**[2], **M. Amparo F. Faustino**[1], **Carlos J. P. Monteiro**[1]

[1]LAQV-Requimte e Departamento de Química, Universidade de Aveiro, 3010-193 Aveiro, Portugal.
[2]CESAM, Departamento de Biologia, University of Aveiro, 3810-193 Aveiro, Portugal.
**sofia.sarabando@ua.pt*

As sulfonamidas são uma classe de antibióticos que atuam como inibidores competitivos da enzima bacteriana diidropteroato sintase, mimetizando o ácido *p*-aminobenzoico (PABA) e, consequentemente, inibindo a síntese de ácido tetra-hidrofólico [1]. A sua atuação impede assim que o ADN bacteriano seja replicado, e não ocorre crescimento nem divisão celular. No entanto, a ligação das sulfonamidas a esta enzima é reversível, pelo que as bactérias podem adquirir resistência a esta classe de antibióticos [2].

A Terapia Fotodinâmica Antimicrobiana (aPDT) é uma técnica multialvo, que envolve a administração de um fotossensibilizador (PS), luz visível e dioxigénio e surge como uma alternativa aos antibióticos convencionais, pois permite a inativação bacteriana sem que os estas desenvolvam mecanismos de resistência [3]. Quando PS é fotoativado, ocorre produção de espécies reativas de oxigénio (ROS) que determinam a morte celular. As porfirinas são macrociclos tetrapirrólicos geradores de ROS e, têm sido utilizadas com sucesso como PS em PDT [4]. Mais recentemente foi demonstrado que a administração concomitante de PS e sais inorgânicos, como KI, resulta geralmente no aumento da taxa de inativação bacteriana quando comparada com a utilização isolada de PS [5,6]. Assim, este estudo teve como objetivo a preparação e caracterização de três novas *meso*-tetraarilporfirinas funcionalizadas com grupos sulfonamida e a avaliação de propriedades biológicas destes novos derivados combinados com KI na inativação de bactérias de *Staphylococcus aureus* resistente à meticilina (MRSA).

Os estudos fotodinâmicos revelaram que todos os PS preparados foram eficazes na fotoinativação de MRSA, sendo a 5,10,15,20-tetrakis(4-sulfofenil)porfirina o PS que apresentou maior eficácia. A associação dos PS com KI mostrou-se vantajosa, potenciando o efeito fotodinâmico dos PS, reduzindo o tempo de inativação bem como da concentração de PS necessária para inativar MRSA. Nesta comunicação serão apresentados e discutidos a síntese e caracterização dos novos derivados bem como os resultados biológicos obtidos sobre MRSA.

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New hexadentate Fe chelator: an EPR study to access chelator interaction with liposome membrane models

<u>Sílvia Vinhas</u>[1,*], Baltazar de Castro[1], Maria Rangel[2]

[1]REQUIMTE-LAQV, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007, Porto, Portugal
[2]REQUIMTE-LAQV, Instituto de Ciências Biomédicas Abel Salazar, Rua Jorge Viterbo 228, 4050-313, Porto, Portugal
**silviavinhas@fc.up.pt*

Metal ions are crucial for a plethora of biological processes. Transition metal ions, mainly due to the high number of possible oxidation states, are advantageous in terms of electron's exchange. However, the low solubility of metal ion's natural form (normally hydroxide), represent a drawback in terms of bioavailability. Nature developed mechanisms to increase the bioavailability of the required metal ion. One of its strategies includes the biosynthesis of specific organic compounds, capable to bind metal ions (e.g., porphyrins, siderophores, etc) [1]

Iron is one of the most abundant transition metal ions on earth, intervening in several biochemical processes in different living organisms. However, several diseases related with the loss of Fe homeostasis have been identified on humans. For that reason, there is an urgent need of new molecules that can correct Fe levels in the body and our group is focused on the design of metal ion chelators and metal on chelates for application I health, agriculture and environmental application chelators.[2,3]

Labelling membrane mimetic models with spin labels allows the identification of induced membrane perturbations through Electron Paramagnetic Resonance. The use of spin probes at different depths is a well stablish method to extract information regarding the environment of the studied spin label.[4]

In this work we describe the synthesis and the evaluation of the permeation properties of three Fe chelators (CP256, MRHT0 and MRHTN) over three membrane mimetic models (liposomes). These liposomes aim to mimic vegetal cell membrane, bacteria cell membrane and animal cell membrane in order to cover the potential areas of application. Liposomes were labelled with 5-DSA and 16-DSA spin labels to allow the study using Electron Magnetic Resonance. Results showed different permeation properties of the chelators towards each formulation and provided information regarding permeation properties.

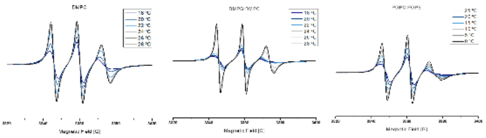

Figure 5 - Temperature gradient of 16-DSA spin label signal on DMPC, DMPG:DMPC and POPC: POPE membrane mimetic liposomes.

Agradecimientos

This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the project UIDB/50006/2020 | UIDP/50006/2020. SV is grateful to NORTE-08-5369-FSE-000050 for her PhD grant.

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Pharmaceutical cocrystals: Design approaches

Rui Ferro[1], Al Mohtar[2], João F Pinto[1], João A Lopes[1]

[1]Institute for Medicines Research (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal
[2]CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal.
**rui.ferro@campus.ul.pt*

Overcoming poor bioavailability is still a pivotal step when implementing new oral form therapeutics [1]. Multicomponent-systems, like cocrystals, have the potential to modulate the characteristics of the active pharmaceutical ingredient [API] and drug product [2,3]. Approaches that rely on these systems present a promising, but still barely explored strategy to overcome poor bioavailability and other API, pharmaceutical formulations components and manufacturing related obstacles [4–6]. Although their potential has been proven, implementation of such technologies by the pharmaceutical industry has some limitations namely, the screening process for new cocrystals is a painstaking and time-consuming task still grounded on a trial-and-error empirical approach. Common issues include coformers selection, formulation design, poor shelf life stability, manufacturing technology to be considered [7]. A search for "*pharmaceutical cocrystals*" on PubMed.gov (Fig.1) has shown that the majority of the published reports consider some sort of computational methods employed in the research published reflecting the increasing willingness of the scientific community to consider the use of such methodology on developing a new cocrystal. However, it was also observed that a large number of studies failed to consider computational methods to their full potential, i.e., the studies report the use of one or two techniques or, simply as a minor complementary tool to the empirical techniques considered. Furthermore, a large number of studies, designed on an empirical basis or based on hybrid approaches, use a small pool of molecules tested which might hinder the relevance of the results [8]. The scope of this work is to implement different computational methods and physical characterization techniques on a large pool of well-studied cocrystals models (different combinations of APIs and coformers) and to unveil critical parameters in the process of screening, towards the prediction and selection of cocrystals with better biopharmaceutical characteristics for a shorter research time needed to manufacture new cocrystals.

Table 1. Data from 101 articles and research papers published in 2021[8]

Exclusively Empirical studies	46
Mostly Empirical studies	13
Empirical and Computational studies	38
Exclusively computational studies	3
Average number of cocrystals studied	≈2
Average number of APIs studied[a]	≈1

[a]in studies that used more than one cocrystal (43 studies)

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Cytotoxicity induced by 3’,4’,7-trihydroxyflavone derivatives in *in vitro* models of osteosarcoma

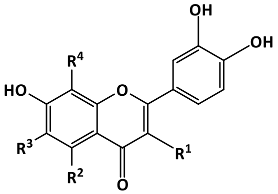
José Miguel P. Ferreira de Oliveira[1,*], **Ana Teresa Rufino**[1], **Carina Proença**[1], **Eduarda Fernandes**[1]

[1]LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
*jmoliveira@ff.up.pt

Osteosarcoma (OS), the most common bone cancer, is currently treated with a sequence of neoadjuvant therapy, tumor resection, and adjuvant therapy [1]. In the event of recurrence, chemotherapy is limited by poor overall survival rates, thus, novel therapeutic agents are urgently needed. Recently, flavonoids have been described to inhibit OS development [2], which suggests their positive effects in OS therapy.

The present study aimed to evaluate the *in vitro* cytotoxicity of a group of 3’,4’,7-trihydroxyflavones in OS. For this purpose, the MG-63, Saos-2, HOS, and 143B OS cell lines were treated with flavonoids (Figure 1), 10 – 160 µM, for 48 h. Then, WST-8 and sulforhodamine B assays were performed to estimate cell viability and growth. The most active compound was investigated for induction of apoptosis in MG-63 cells. Apoptosis was evaluated in line with induction of phosphatidylserine externalization (annexin V assay, 24h, and 48h), Bax and caspase-3 levels (Western blot, 24h), and caspase-3 activity (colorimetric assay, 14h, and 24h).

Compared to 3’,4’,7-trihydroxyflavone (**1a**), all derivatives were more potent in decreasing OS cell viability and inhibiting growth. Additional hydroxylation, especially at C-5 and C-8 of the A-ring, most efficiently decreased OS cell viability. Gossypetin (**1g**), the strongest inhibitor, induced apoptosis in the MG-63 cell line. Apoptosis induction was associated with increased caspase-3 levels and activity and with an increase in the pro-apoptotic factor Bax. These results indicate that gossypetin displays positive effects in OS therapy *in vitro.* Additional studies are required to clarify the potential cellular effects of this flavonoid in human OS.



1a: R^1, R^2, R^3, R^4 = H (3',4',7-Trihydroxyflavone)
1b: R^1 = OH, R^2, R^3, R^4 = H (Fisetin)
1c: R^1, R^3, R^4 = H, R^2 = OH (Luteolin)
1d: R^1, R^2, R^4 = H, R^3 = OH (3',4',6,7-Tetrahydroxyflavone)
1e: R^1, R^2, R^3 = H, R^4 = OH (3',4',7,8-Tetrahydroxyflavone)
1f: R^1, R^2 = OH, R^3, R^4 = H (Quercetin)
1g: R^1, R^2, R^4 = OH, R^3 = H (Gossypetin)

Figure 1. 3’,4’,7-Trihydroxyflavone derivatives investigated by cytotoxicity screening

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Acknowledgments
The authors acknowledge the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-029243) and National Funds (FCT, Fundação para a Ciência e Tecnologia) for the funds received through project PTDC/MED-QUI/29243/2017. ATR and CP thank FCT for the funding through the project PTDC/MED-QUI/29243/2017. JMPFO thanks FCT for funding through program DL 57/2016 – Norma transitória (ref. SFRH/BPD/74868/2010).

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Can infrared analysis of blood plasma assist diagnosis of respiratory viral infection

Nádia Aguiam, Carolina Piedade, Alexandra Martins, Carlos Araújo, João Gonçalves, João A Lopes

Institute for Medicines Research (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal
*nadia.*aguiam@campus.ul.pt*

Concern on the public health and social impact of respiratory viral infections boosted when the first cases of COVID-19 were diagnosed, and viral infection severe impact was confirmed. Even though during 2021 and 2022 with the generalized administration of vaccines, the COVID-19 pandemic was mostly controlled, it becomes clear that challenges are far from over. Recent evidence shows that the impact of influenza, COVID-19 and RSV mostly, have the potential to disturb at a great extent and again increase the overall death rate during the typical respiratory viral infection season spreading from November to February in the north hemisphere. RSV in particular affects mostly children which increases the concerns and triggers again substantial public awareness on this problem. [1,2]

While it is currently fast to diagnose the presence of the virus, it is still difficult to predict the evolution of the infection and its potential to cause severe impact on the patient.[3,4]

Fast diagnosis methods to assist medical estimation of disease progression became one of the most important goals of the scientific community. In this context, several approaches have been attempted. Within the palette of potential approaches, infrared spectroscopy of blood plasma emerges as an interesting possibility given the speed a result can be obtained and the relative low cost per analysis and simplicity of execution. [4-6]

This communication addresses the potential of infrared spectroscopy for assisting viral infection prognosis. Presented results are based on multiple studies conducted between 2020 and 2022 in the context of the COVID-19 disease. Potential of the technique was evaluated in terms of the analytical performance and medical diagnosis tool.

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QUÍMICA TEÓRICA

Interface between BmimPF$_6$ ionic liquid and gold metal surface from MD simulations perspective

Iuliia V. Voroshylova[1], Heigo Ers[2], Borja Docampo Álvarez[2], Piret Pikma[2], Vladislav B. Ivaništšev[2], M. Natália D.S. Cordeiro[1]

[1]LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]Institute of Chemistry, University of Tartu, Ravila 14a, Tartu 50411, Estonia
voroshylova.iuliia@fc.up.pt

Differential capacitance (C) is one of those rare interfacial properties that can be measured experimentally, derived theoretically, and modeled computationally. It plays the key role in the theories of the electrical double layer (EDL), as C describes the magnitude of electrolyte response to the variation of surface charge density (σ) due to change in the electrode potential (U). Additionally, differential capacitance is in the heart of modern technologies: supercapacitors, capacitive sensors, thin-film transistors, and actuators, are developed with regard to C [1,2]. Contrarily to the dilute electrolytes, for which the basic theory behind the solid-liquid interface has been established, the EDL between metal surfaces and concentrated electrolytes, including ionic liquids (ILs), represents a challenge for theory [3,4], mainly because of the surface charge screening. Due to high charge concentration, ILs overscreen the surface charge and organizes in alternating layers of anions and cations next to the electrode.

In this work, we performed molecular dynamics (MD) simulations of the Au(100)|BMImPF$_6$, Au(110)|BMImPF$_6$ and Au(111)|BMImPF$_6$ interfaces using the constant field method and extensive systematic sampling in a wide potential window. We have thoroughly considered the following aspects: i) influence of various mathematical approaches for treatment of the simulated data; ii) influence of the gold electrode crystallography on the differential capacitance; iii) the impact of the surface charge plane position in the MD trajectory treatment on the magnitude of capacitance curve; iv) the number of capacitance peaks and their structural origins; v) the influence of potential scan direction on the formation of interfacial structures, that may result in capacitance-potential hysteresis [5-7].

Funding

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The Reaction Mechanism of SARS-CoV-2 Spike Protein Cleavage by TMPRSS2: A Quantum Mechanics/Molecular Mechanics Study

Luís M. C. Teixeira[1], João T. S. Coimbra[1], Maria João Ramos[1], Pedro A. Fernandes[1*]

[1]LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
**corresponding author: pafernan@fc.up.pt*

Since COVID-19 was declared an international pandemic, several efforts have been made to control the spread of the SARS-CoV-2 virus. Nowadays, despite the development of vaccines against the virus, there is still an urgent need to develop efficient drugs to treat infected patients. Thus, understanding the biological mechanisms that govern viral infection is essential as it can be helpful in the development of novel therapeutic drugs [1]. An attractive drug target is the transmembrane protease serine 2 (TMPRSS2), a physiological enzyme that plays a vital role in the SARS-CoV-2 infection mechanism. TMPRSS2 promotes a proteolytic cleavage on SARS-CoV-2 Spike (S) protein, culminating in a required conformational change that facilitates host-cell entry [2]. Having in mind that the information retrieved from quantum mechanics/molecular mechanics (QM/MM) studies could be important in the design of transition-state (TS) analogues inhibitors, we used multiscale QM/MM calculations to the determine the mechanism behind the rate-limiting acylation stage of the proteolytic cleavage of the S protein. Our calculations showed that acylation occurred in two sequential steps: i) a nucleophilic attack from Ser441 to the substrate's P1-Arg concerted with a proton transfer to His296, and 2) a proton transfer from His296 to the Substrate's P1'-Ser concerted with the cleavage of the P1-P1' peptide bond. The two steps had a Gibbs activation energy of 17.1 kcal/mol and 15.8 kcal/mol, respectively (**Fig.1)**. An oxyanion hole stabilized the rate-limiting TS by 8 kcal/mol. An analysis of the interactions present at the tetrahedral intermediate pointed out specific ways to construct higher-affinity non-covalent transition-state analogue inhibitors with the potential to be used as therapeutics against SARS-CoV-2.

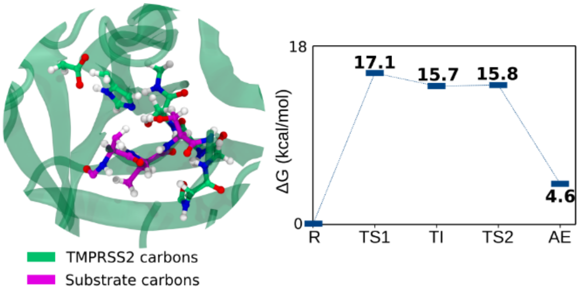

Fig.1. On the left, we depict the atoms of the QM region in sticks and coloured by atom type. The TMPRSS2 carbon atoms are coloured in green, whereas the substrate's carbon atoms are coloured in magenta. On the right, we show the free energy profile for the acylation step catalysed by TMPRSS2 (R, Reagents; TS, Transition-State; TI, Tetrahedral Intermediate; AE, Acyl-Enzyme).

Acknowledgements

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(Non)-Polarizable models for magnetic ionic liquids

Nádia M. Figueiredo[1,*], **Jorge C. M. Marques**[2], **M. Natália D. S. Cordeiro**[1]

[1] Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal
**up201006255@up.pt*

Magnetic ionic liquids (MIL) are a subclass of task-specific ionic liquids that contain a paramagnetic element (metal transition or lanthanides atoms) in their structure and thus acquires magnetic properties when a magnetic field is applied.[1] This feature makes the MILs reusable by magnetic separation and further improves their transport, reducing their viscosity and increasing their mobility in presence of the external magnetic field.[2] Further, these compounds retain all desirable characteristics of ionic liquids such as low melting points and flammability, insignificant vapor pressure, high thermal stability, etc, and their tunability as well. Therefore, the carefully designed structure of the MILs has led to the development of magnetoactive compounds that have unique physicochemical properties.

These magnetoactive compounds were first synthesized in 2004 and have shown promise in several applications, including catalysis, gas absorption, analytical extractions, and sensing. However, computational studies, in particular molecular dynamics (MD) simulations, are scarce, which is probably due to the lack of field forces for these compounds.[3,4]

In this work, non-polarizable and drude-polarizable models are set-up for [FeX_4]-based MILs, where X = Cl and Br atoms, in order to study their thermodynamic, dynamic, and structural properties (Fig.1) through MD simulations. Based on this study, we will be able to achieve a thoughtful understanding of these MILs and their efficient mixtures, as well as propose a rational design of MILs that will enhance their applications.

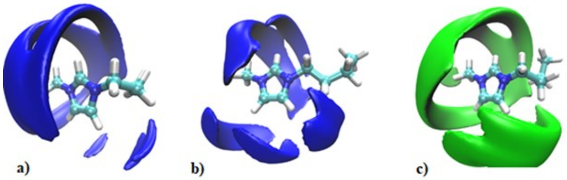

Fig.1. Spatial distribution functions of a) [Emim][FeCl4], b) [Bmim][FeCl4], and c) [Bmim][FeBr4] describing the distribution of [FeCl4] (blue) and [FeBr4] (green) anion around the reference cation at 293.15 K.

Acknowledgments

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Interface between $BmimPF_6$ ionic liquid and gold metal surface from MD simulations perspective

Iuliia V. Voroshylova[1], Heigo Ers[2], Borja Docampo Álvarez[2], Piret Pikma[2], Vladislav B. Ivaništšev[2], M. Natália D.S. Cordeiro[1]

[1]LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]Institute of Chemistry, University of Tartu, Ravila 14a, Tartu 50411, Estonia
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Composición lipídica alterada provocada por COVID en fase aguda y persistente y la influencia del sistema inmune innato: Un estudio de Dinámica Molecular

Alejandro S. González[1], **Ángel P. Guillén**[2], **Rebeca G. Fandiño**[1]

[1]Departamento de Química Orgánica, Center for Research in Biological Chemistry and Molecular Materials,
Universidade de Santiago de Compostela, Campus Vida s/n, E-15782 Santiago de Compostela, España
[b]Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago de Compostela, E-15782,
Santiago de Compostela, Spain
**alejandro.seco@rai.usc.es*

En la era post-pandémica en la que nos encontramos, existe una condición conocida como COVID persistente (Long-COVID), que está afectando a un número cada vez mayor de personas. Se calcula que alrededor del 10-20% de los pacientes que han sido infectados no se recuperan completamente y experimentan estos síntomas persistentes incluso meses después de haber superado la enfermedad. [1, 2]

Desde el comienzo de la pandemia se han invertido grandes esfuerzos en secuenciar el ARN del virus e investigar las proteínas de su membrana para acelerar la creación de vacunas. Sin embargo, existen factores igual de importantes que han recibido menos atención. Un ejemplo es el perfil lipídico de los pacientes con COVID-19, que resulta alterado no sólo durante la fase aguda sino también durante la evolución de la enfermedad e incluso está presente en pacientes con secuelas a medio plazo. [3,4] En un artículo reciente [5] de nuestro grupo de investigación, se sugiere una relación entre los perfiles lipídicos de los pacientes con COVID-19 y el propio sistema inmune innato, a través de los péptidos antimicrobianos (AMPs), siendo una posible causa de la sobreinflamación que provoca la enfermedad.

Para entender cómo interactúan los diferentes péptidos antimicrobianos con las membranas celulares alteradas por la COVID-19, utilizaremos simulaciones de Dinámica Molecular. En este trabajo presentaremos los primeros resultados de esta investigación, enfocada a entender el mecanismo de acción de estos péptidos a nivel molecular cuando las membranas celulares están alteradas como consecuencia de la COVID persistencia.

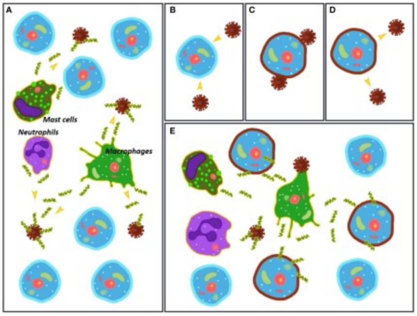

Fig.1. Secuencia de como el virus al infectar una célula, esta cambia su composición de membrana, quedando "marcada" y siendo reconocida como extraña ante nuestro sistema inmune innato.

Agradecimientos

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Back to the Chirality in Coarse-Grained Cyclic Peptides: The Ma(R/S)tini parametrization

Alfonso Cabezón[1,*], Martín Calvelo[2], Ángel Piñeiro[3] and Rebeca García-Fandiño

[1]Departamento de Química Orgánica, Center for Research in Biological Chemistry and Molecular Materials, Universidade de Santiago de Compostela, Campus Vida s/n, E-15782 Santiago de Compostela, Spain
[2]Departament de Química Inorgànica i Orgànica (Secció Química Orgànica) & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain
[3] Departamento de Física de Aplicada, Facultade de Física, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain
*alfonsocabezon.vizoso@usc.es

Cyclic Peptides (CPs) have arisen as a promising class of potential Antimicrobial Peptides (AMPs) since they share with conventional AMPs the ability to distinguish bacteria from healthy cells based on the lipidic composition, but their cyclic structure provides them increased resistance to protease degradation. CPs formed by alternation of D- and L-amino acids present planar structures that can self-assemble into nanotubes by means of parallel or antiparallel β-sheets, the active species, especially in the presence of lipidic membranes[1].

However, current experimental techniques cannot reach the molecular level of resolution needed to get to a full understanding of their mechanisms of action. In this respect, Molecular Dynamics (MD) simulations can provide useful insights about the behaviour of these systems[2]. Nevertheless, the timescale expected for the self-assembly cannot be addressed with classical MD simulations and approximations are needed. In this regard, Coarse-Grain (CG) resolution has been employed. However, this approximation leads to the loss of D/L chirality and therefore, the specific directionality of their interaction. To tackle this issue, the general CG Force Field Martini, has been modified to introduce directionality on the CPs aiming at a more realistic representation (Fig. 1). The so-called Ma(R/S)tini can reproduce experimental and structural data obtained in the wet-lab[3] as well as the correct trends for CPs with different amino acid sequences. This work could lead to a deeper understanding of such processes and more rational designs in the future.

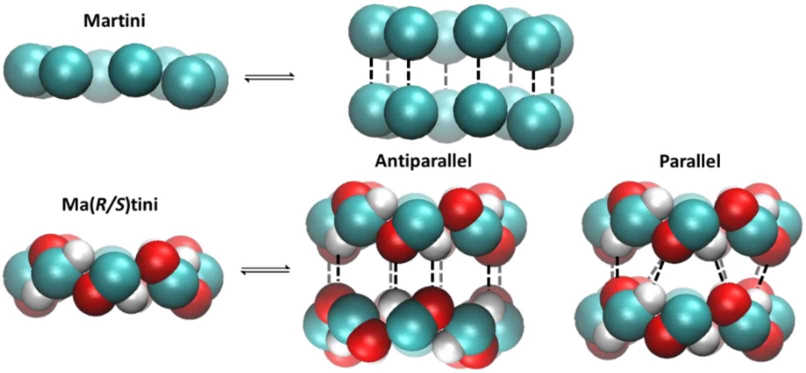

Fig.1. Comparison of the interactions between CPs in the Original Martini Force Field and the modified version

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Exploring innate immune system peptides and their cell membrane interactions

Daniel Conde[1, *], Martín Calvelo[2], Ángel Piñeiro [1], Rebeca García Fandiño[2]

[1]Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago de Compostela,
15782 Santiago de Compostela, Spain
[2]Center for Research in Biological Chemistry and Molecular Materials, Departamento de Química
Orgánica, Universidade de Santiago de Compostela, Campus Vida s/n, 15782 Santiago de
Compostela, Spain
**danielconde.torres@usc.es*

Cancer, ageing and infection have traditionally been treated almost as independent compartments, ignoring or downplaying the interconnections between them. However, a growing number of studies suggest that a lipid alteration in the cell membranes is a point of intersection in these pathologies [1]. A key part of the innate immune system is Endogenous Therapeutic Peptides (ETPs), short cationic peptides that have the ability to target and disrupt the pathological membranes, which typically contain a high concentration of anionic lipids [2]. Molecular dynamics (MD) simulations are extraordinarily well suited to explore how ETPs interact with membrane models, providing a large amount of information that, nowadays, cannot be assessed by wet-lab methods at the same level of temporal and spatial resolution [2]. However, one of the limitations of conventional MD is that the system can be trapped in local or global minima, which leads to poor sampling of the configurational space. Different methods to escape from energy minima have been developed. Here, we explore the use of one of these methods (Metadynamics) to characterize the interaction between ETPs and different membrane models [3]. As a result, an optimized, reproducible and easy to automate protocol to get the free energy profile corresponding to the interaction between ETPs and lipid bilayers is obtained. The protocol here presented is sensitive both to the ETP sequence and the lipid composition of the membrane model.

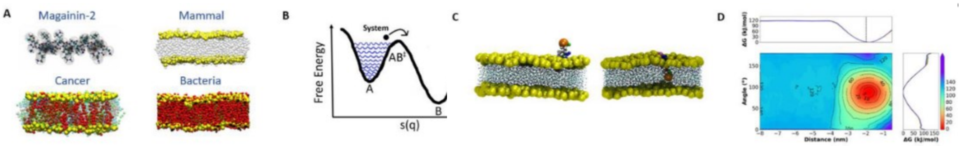

Fig.1. Schematic graphic representation of the work performed. A) ETP (Magainin-2) and membrane models use in the study. B) Example of a sampling optimization algorithm based on MD (Metadynamics) that allows exploration of a space of conformations defined by the selected collective variables. C) Snapshot of a Metadynamics simulation that would not be observed in a standard MD simulation. D) 2D-Graphical representation of the interaction potential energy surface (PMF) obtained in one of the systems used.

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QUÍMICA ALIMENTARIA

Obtención de lípidos polares a partir de desechos industriales de pulpo (*Octopus vulgaris*) mediante empleo de disolventes de tipo GRAS

Santiago P. Aubourg[*], **Manuel Iglesias, Raquel Costa, Marcos Trigo, Mª. Jesús González, Salomé Lois e Isabel Medina**

Departamento de Ciencia y Tecnología de Alimentos, Instituto de Investigaciones Marinas (CSIC), Vigo, España
**saubourg@iim.csic.es*

Como resultado de la comercialización de las especies marinas se genera una cantidad importante de desechos (cabezas, vísceras, sangre, piel, etc.) que son portadores de constituyentes susceptibles de ser utilizados en nutrición, farmacia y cosmética [1,2]. Entre estos constituyentes ha cobrado un interés especial la fracción de lípidos polares debido a su biodisponibilidad, propiedades protectoras y posibilidad de actuar como agentes vehiculares [3]. Asimismo, asistimos en las últimas décadas a un crecimiento importante en el uso de técnicas de extracción de lípidos que reduzcan el grado de contaminación ambiental. Una de estas técnicas es la que emplea disolventes de tipo GRAS (*generally recognised as safe*) al objeto de reemplazar el uso de disolventes agresivos con el medio ambiente [4].

Este estudio se centró en la obtención de lípidos polares a partir del paquete visceral resultante de la comercialización de pulpo común (*Octopus vulgaris*). Esta especia constituye un alimento altamente nutritivo y muy apreciado popularmente, comercializado tanto a nivel artesano como industrial [5]. Para ello, se llevó a cabo un estudio comparativo de la extracción de lípidos totales y fosfolípidos mediante distintas combinaciones de disolventes de tipo GRAS (etanol, EtOH; acetato de etilo, AcOEt; EtOH/AcOEt, 50/50; EtOH/acetona, 50/50). Asimismo, se estudiaron por separado y de forma comparativa los paquetes viscerales grandes (275-325 g) y pequeños (125-150 g). Los resultados fueron comparados con los obtenidos mediante la extracción tradicional empleando una mezcla cloroformo/metanol (1/1).

Como resultado, los sistemas extractores de tipo GRAS reflejaron una recuperabilidad incluida en los rangos 52-63% (vísceras de gran tamaño) y 38-56% (vísceras de pequeño tamaño) al ser comparados con la extracción tradicional. Es de destacar que los valores superiores, en ambos tipos de vísceras, fueron obtenidos mediante uso del sistema EtOH/AcOEt. En lo que respecta a la obtención de fosfolípidos, la comparativa con el método tradicional de extracción indicó valores muy bajos para el sistema AcOEt en ambos tipos de vísceras. Sin embargo, el resto de los sistemas extractores ensayados llevaron a valores incluidos en los rangos 74-86% (vísceras grandes) y 67-75% (vísceras pequeñas). Se concluye el interés en la optimización de la extracción de lípidos polares (fosfolípidos) a partir de desechos comerciales de pulpo mediante el empleo de sistemas disolventes alternativos que sean más respetuosos con el medio ambiente.

Agradecimientos

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ALM34

Use of protective starter cultures and plant essential oils to reduce preservatives in traditional Portuguese sausages: "*Chouriço*" and "*Alheira*"

Arona Pires[1], Raffaella Sanino[2], Silvia Sapio[2], Susana Dias[1,3], Marta Henriques[1,3], Ivo Rodrigues[1,3], Carlos Pereira[1,3*]

[1]Polytechnic Institute of Coimbra, Coimbra Agriculture School, Bencanta, 3045-601 Coimbra, Portugal
[2]University of Naples Federico II. Via Universitá. 96.80055, Portici, Naples
[3]Research Centre for Natural Resources, Environment and Society (CERNAS), Polytechnic Institute of Coimbra, Bencanta, 3045-601 Coimbra, Portugal
**cpereira@esac.pt*

Chouriço is a Portuguese dry-fermented sausage, much appreciated by consumers. It is made with pork meat and fat, coarsely chopped, seasoned with a marinade of wine, salt, garlic, and other optional seasonings, used according to the recipe of each producer. The batter is kept at 4 to 7 °C for 18 to 48 h. It is then stuffed into natural thin pork guts, smoked and matured at a low temperature for 1 to 4 weeks. *Alheira* is a traditional smoked sausage produced in Portugal, naturally fermented, made from boiled meat, (usually pork and/or poultry), and bread. Lactic acid bacteria are the predominant microbiota, but some studies revealed the presence of pathogenic bacteria such as coagulase-positive staphylococci, *Listeria monocytogenes* and *Salmonella* spp.

In the case of *Chouriço,* 5 formulations were tested and compared: conventional (C), with salt containing 5% NO_2 (E250) at the level of 3 g kg^{-1} of the mass; containing Rosao™ (R), a commercial plant extract to replace NO^2; containing a protective starter culture (PC) added at 0.025% of the mixture (Roxanne™) (*Pediococcus acidilactici*, *S. carnosus*, *S. vitulinus* and S. *xylosus*); containing a mixture of *Salvia officinalis* and *Thymus mastichina* 1:1 EOs (EO) added at 0.001%; a combination of PC and EO (EOPC).

In the case of *Alheira*, 4 formulations were tested and compared: conventional (C); containing a protective starter culture (PC) added at 0.025% of the mixture (Trifecta™) (*L. curvatus*, *Pediococcus acidilactici* and *S. carnosus*); containing a mixture of *Salvia officinalis* and *Thymus mastichina* 1:1 EOs (EO) added at 0.001%; containing a combination of PC and EO (EOPC). In both cases, half of the samples were packed in a N_2/CO_2 atmosphere and half under vacuum.

The physicochemical, microbiological and sensory characteristics of the different formulations were evaluated and compared. Although differences in physicochemical characteristics were observed, it was concluded that these differences can be attributed to variations between batters and not to the addition of protective cultures or essential oils, since the added amounts could not interfere with the parameters evaluated. In all formulations of *Chouriço,* Lactococci and Lactobacilli counts were of the order of log 7, and log 8 CFUg^{-1} respectively. Yeasts and molds counts were below log 3 CFUg^{-1}. The counts of coagulase positive Staphylococci were of the order of log 5 CFUg^{-1}. Entereococci counts were below log 4.5 CFUg^{-1}. Vacuum packaging was more efficient than protective atmosphere with relation to *E. coli* counts, without colonies observed. Listeria monocytogenes, Salmonella spp. and sulfite-reducing bacteria spores were not detected. In the case of *Alheira*, Lactococci and Lactobacilli counts were around log 8 CFUg^{-1}, and log 8-9 CFUg^{-1}, respectively. Coagulase positive Staphylococci counts were around log 7 CFUg^{-1}, showing a tendency to decrease over storage. Yeasts and molds counts were around log 5-6 CFUg^{-1} on the first day of storage but increased to log 8-9 CFUg^{-1} at the end of shelf life (60th day of storage). Regarding enterococci and *E. coli* counts*,* the values increased steadily throughout storage. *Listeria monocytogenes*, *Salmonella* spp. and sulfite-reducing bacteria spores were not detected. The sensory impact of EOs can be considered a main constraint, since all samples containing them were differentiated by the sensory panel.

It was concluded that the amount of protective cultures used must be increased to overcome the harsh conditions occurring during smoking, in which the temperature of the products reaches 50 ºC. Besides, the EOs used must be selected not only for their protective power, but also considering their impact on the sensory characteristics of the products, in order to avoid undesirable impacts in the flavor of the products.

Acknowledgments

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Evaluation of the physico-chemical, microbiological and sensory characteristics of sheep's and goat's ice cream, produced with UF concentrated second cheese whey

Arona Figueroa Pires[1,2*], **Olga Díaz Rubio**[2], **Angel Cobos Garcia**[2], **Carlos Dias Pereira**[1,3]

[1] Polytechnic Institute of Coimbra, College of Agriculture, Bencanta, 3045-601 Coimbra, Portugal;
[2] Faculty of Sciences of Lugo, Department of Analytical Chemistry, Nutrition and Bromatology, Food Tech-nology Area, Universidade de Santiago de Compostela, E-27002 Lugo, Spain
[3] Research Centre for Natural Resources, Environment and Society (CERNAS), Bencanta,3045-601 Coimbra, Portugal
**arona@esac.pt*

The development of new food products that promote consumer's health has always been of great interest. The dairy industry is perhaps the best example regarding the emergence of new products with claimed health benefits. Second cheese whey (SCW) is a by-product of whey cheese manufacture and contains potential ingredients for the development of food products with improved nutritional characteristics and other functionalities. However, SCW is usually treated as waste or as animal feed. Nowadays, due to their nutritional quality, whey products have gained a prominent position among healthy food products [1].

In this work, sheep's and goat's liquid second cheese whey concentrates (LSCWC's) obtained by ultrafiltration (UF), were used as raw materials to produce frozen yoghurts, using a conventional yoghurt starter, a kefir culture, and a mixture of probiotic cultures. Frozen sheep and goat yoghurts presented significant differences concerning physicochemical (dry matter, protein, fat, minerals, pH and acidity) and microbiological analyses (*Lactobacilli sp. and Lactococci sp.*). These properties were evaluated at days 1, 30, 60 and 120. Overrun and meltdown rate of the different products were also evaluated and compared.

Regarding the sensory acceptance, both products showed encouraging results. The sheep-based frozen products were better accepted by consumers.

Frozen products containing probiotics maintained high counts of both types of microorganisms until the end of storage.

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Comparison of the amino acid profile of two by-products of the coffee industry: pulp and husk

Marlene Machado[1,*], **Susana Machado**[1,2], **Helena Ferreira**[3], **M. Beatriz P. P. Oliveira**[1], **Rita C. Alves**[1]

[1]REQUIMTE/LAQV, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, University of Vigo, Ourense, Spain
[3]REQUIMTE/UCIBIO, Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Portugal
**marlenemachado753@gmail.com*

The transformation of coffee cherries into roasted beans produces a variety of chemically interesting by-products. Dehulling the cherry allows obtaining the by-products coffee pulp and coffee husk, depending on the method used, wet or dry, respectively [1]. Previous studies on coffee pulp or coffee husk have focused mainly on the profile of phenolic compounds and their antioxidant activity [1,2,3]. Important amino acids are also present in these by-products [2], however, studies on their profile in coffee pulp and husk are still limited [2]. The amino acid composition is essential to estimate not only the real protein content, but also the protein quality of coffee husk and pulp [4]. Thus, the aim of this study was to compare the amino acid profile of two coffee by-products: coffee pulp (*Coffea arabica*, from Colombia) and coffee husks (*Coffea canephora*, from Panama). Dried samples were kindly provided by Colombian and Panamanian producers through a national coffee importer and roaster company (JMV-José Maria Vieira, SA).

For tryptophan quantification, samples were hydrolyzed under alkaline conditions (4 M KOH, 110 °C, 4h). For the remaining amino acids, acid hydrolysis (6 M HCl, 110 °C, 24h) was performed. Analyses were performed in triplicate. The hydrolysates were neutralized, submitted to an automated online derivatization with OPA and FMOC and analyzed by RP-HPLC/FLD. Amino acids were identified by comparing their retention times with those of known standards and quantified by the internal standard method using calibration curves obtained for each compound [4].

The results show that coffee by-products contain a variety of essential and non-essential amino acids. Except for aspartic acid, all the amino acids were significantly higher ($p<0.05$) in the coffee pulp. Leucine was the main essential amino acid determined (4.08 ± 0.26 and 2.35 ± 0.11 mg/g dry weight [dw] for pulp and husks, respectively). Regarding non-essential amino acids, aspartic acid predominated (6.63 ± 0.44 and 7.50 ± 0.56 mg/g dw for pulp and husks, respectively). The sum of total amino acid (∑TAA) refers to the true protein content of by-products. Coffee pulp (50.35 ± 2.91 mg/g dw) showed a significantly higher ($p<0.05$) ∑TAA compared to coffee husks (35.64 ± 1.56 mg/g dw).

In conclusion, both by-products could be a potential source of essential and non-essential amino acids. The consumption of coffee pulp and husk should be promoted due to the richness in bioactive compounds, but also to answer the circular economy and sustainability issues.

Agradecimientos

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Enfoques integrados para el impulso socioeconómico de la producción y consumo sostenible de hongos de Montesinho

Ana Saldanha,[1,2,3] Leonardo Corrêa Gomes,[1,2] José Pinela,[1,2] Manuel A. Coimbra,[3] Lillian Barros,[1,2] Maria Inês Dias,[1,2*] Carla Pereira[1,2]

[1] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;*
[2] *Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.*
[3] *LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.*
**maria.ines@ipb.pt*

El Parque Natural de Montesinho representa un área de montaña con un patrimonio micológico único. Entre las aproximadamente doscientas setas comestibles que se encuentran en este espacio protegido, la mayoría se consumen desde la antigüedad por su exquisito sabor y valor nutritivo [1]. Sin embargo, la disponibilidad de estos productos de montaña está limitada por su estacionalidad y condiciones climáticas, cuestión que se intensifica con el cambio climático. Por otro lado, las prácticas insostenibles de recolección de hongos y el comercio ilegal de especies de alto valor también han sido prácticas comunes con impactos negativos en el ecosistema y la economía regional y nacional. Todas estas cuestiones, junto con la incapacidad de los recolectores locales para garantizar la autenticidad/inocuidad de las setas recolectadas, han llevado a muchos restaurantes a evitar su inclusión en sus menús, salvaguardando su negocio y la salud de los consumidores. Así, se propone la producción de apreciados hongos comestibles en ambiente controlado *ex-situ*. Se está realizando una extensa caracterización nutricional, química y biológica para asegurar la alta calidad de las especies producidas y la preservación de sus características originales. El desarrollo de un sello de calidad y seguridad, “Safe2Taste”, que garantiza la trazabilidad de toda la cadena de producción, tiene como objetivo aumentar la confianza/fidelidad de los consumidores en los productos.

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Antioxidant capacity of *Palaemon serratus* and *Palaemon varians* shell waste

Maria Luz Maia[1],* Fátima Barroso[1], Clara Grosso[1], Cristina Delerue-Matos[1], Valentina Fernandes Domingues[1]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, 4249-015 Porto, Portugal
**mariadaluz.maia@gmail.com*

Seafood is highly consumed and appreciated all over the world. Shrimps are a type of seafood considered as high-quality food and as part of a balanced diet. Over the years the shrimp market has been grown, making the shrimp a valuable source of nutrients to the human population [1].

The companies that process shrimps generate massive amounts of shrimp bio-waste (shrimp shells) during handling. Approximately 50% by weight of raw shrimp are considered waste. The disposal of this waste contributes to environmental and health problems. So it is important to convert this shell waste in new value added products [2]. So, the main objective of this work was to assess the possibility to discover added nutritional value from shell wastes obtained from two shrimp species, *Palaemon serratus* and *Palaemon varians* harvested from the Portuguese coast.

For that purpose, *P. serratus* was gathered in Figueira da Foz and Vila do Conde and *P. varians* from wild and aquaculture origin in Sado estuary. Sampling was carried out in autumn and spring between 2017 and 2019 and the shell was separated from the edible portion of the shrimp and stored at -20 ºC until analysis. The antioxidant capacity of shrimp shell waste was determined through the analysis of total phenolic content (TPC), ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picryl-hydrazyl-hydrate free radical scavenging ($DPPH^{\bullet}$) and 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) radical scavenging activity ($ABTS^{\bullet+}$).

The results revealed significant differences between shrimp species. TPC differed between 8.59 mg gallic acid equivalents (GAE)/g dry weight (dw) in *P. serratus* to 7.12 mg GAE/g dw in *P. varians*. $ABTS^{\bullet+}$ scavenging activity values were 5.95 mg trolox equivalents (TE)/g dw and 7.38 mg TE/g dw for *P. serratus* and *P. varians*, respectively. For $DPPH^{\bullet}$ the values ranged from 0.53 mg TE/g dw for *P. serratus* to 0.79 mg TE/g dw for *P varians*. Regarding the influence of the sampling season onto the antioxidant capacity, differences between seasons were also noticed. The values were higher in autumn, 9.67 mg GAE/g dw (TPC), 6.32 mg TE/g dw (FRAP) and 0.76 mg TE/g dw ($DPPH^{\bullet}$), whereas for spring the values were 6.04 mg GAE/g dw, 4.72 mg TE/g dw and 0.56 mg TE/g dw for the same assays. Concerning the sampling locations, differences were also found for TPC, $ABTS^{\bullet+}$ and $DPPH^{\bullet}$ values. Shrimp shell waste from Figueira da Foz exhibited the highest values of TPC (8.78 mg GAE/g dw) and $ABTS^{\bullet+}$ (6.74 mg TE/g dw) and from Sado estuary displayed the strongest $DPPH^{\bullet}$ scavenging activity (0.79 mg TE/g dw).

This study is important to recognize the quality and possible added value of shrimp waste understanding the differences between species, seasons, and locations for the potential incorporation of this waste into different new products.

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Perfil fenólico e avaliação da atividade antioxidante e antimicrobiana do epicarpo de *Sicana odorifera* (Vell.*)* Naudin

Bianca R. Albuquerque[1,2,3*], Maria Inês Dias[1,2], Jovana Petrović[4], Marina Soković[4], M. Beatriz P. P. Oliveira[3], Isabel C.F.R. Ferreira[1,2], Lillian Barros[1,2,*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] REQUIMTE—Science Chemical Department, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[4] Institute for Biological Research “Siniša Stanković”, Department of Plant Physiology, University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia
**lillian@ipb.pt*

As frutas tropicais são amplamente apreciadas pelo seu sabor adocicado e geralmente conhecidas pela sua composição rica em compostos bioativos. No entanto, o processamento deste tipo de fruta pode gerar uma grande quantidade de subprodutos não comestíveis e não comercializáveis, constituídos principalmente por cascas e sementes. Estes subprodutos foram já descritos como tendo maior quantidade de compostos bioativos do que as partes comestíveis; com isto, o interesse por parte da comunidade científica e também de diversas áreas industriais para a valorização destes subprodutos tem vindo a aumentar exponencialmente [1]. Neste contexto, o epicarpo rígido e de coloração roxa intensa não comestível de *Sicana odorifera* (Vell.) Naudin, uma fruta tropical do Brasil [2], foi avaliado quanto à sua composição fenólica, incluindo antocianinas, por Cromatografia Líquida de Alta Performance acoplada a um detetor de díodos e um espectrómetro de massa acoplado a uma fonte de ionização por *eletrospray* (HPLC-DAD/ESI-MSn). A bioatividade do extrato hidroetanólico foi também avaliado através de *ensaios in vitro,* como: a atividade antioxidante, determinada pelo ensaio de substâncias reativas ao ácido tiobarbitúrico (TBARS) e pelo ensaio de inibição da hemólise oxidativa (OxHLIA), e a atividade antimicrobiana, testada em quatro estirpes bacterianas e quatro fúngicas pelo método de microdiluição.

O extrato hidroetanólico do epicarpo de *S. odorifera* apresentou quatro compostos fenólicos, a saber, dois derivados de quercetina e kaempferol e duas antocianinas, nomeadamente a pelargonidina 3-*O*-glucósido e a cianidina 3-*O*-glucósido, sendo o grupo das antocianinas o mais abundante com uma quantidade total de 24 ± 1 mg de antocianinas/g de epicarpo seco. Em relação ao seu potencial bioativo, o extrato hidroetanólico de *S. odorifera* revelou uma atividade antioxidante considerável (valores EC_{50} = 48,2±0,5 e 27±1 µg/mL para os ensaios TBARS e OxHLIA, respetivamente) e ação antimicrobiana contra todas as estirpes de bactérias e fungos avaliadas (concentração mínima inibitória (CMI) ≤ 2,2 mg/mL).

Os resultados obtidos permitem destacar o epicarpo desta fruta tropical como uma fonte potencial de compostos bioativos com grande valor de mercado, uma vez que podem ser aplicados em diversos setores industriais, incluindo a indústria alimentar e farmacêutica.

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Extraction of bioactive compounds from three varieties of date by-products through sustainable methodologies

Mariño-Cortegoso, Sandra[1*], **Rodríguez Bernaldo de Quirós, Ana[1]**, **Sendón, Raquel[1]**, **Barbosa-Pereira, Letricia[1]**

[1]Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Pharmacy,
University of Santiago de Compostela, Santiago de Compostela, Spain
**sandra.marino.cortegoso@usc.es*

Date pits are considered by-products during fruit processing, though being a rich and low-cost source of polyphenols with antioxidant activity, which may be revalorized as food ingredients or additives to reduce food waste in a circular economy concept. This study aimed to recover high-added value compounds, mainly polyphenols, from three varieties of date seed palms (Allig, Kentichi and Deglet Nour) using sustainable methodologies for further food applications.

Ultrasound-assisted extraction (UAE) was selected for the optimization. The parameters optimized were the extraction time, the percentage of ethanol (v/v) and the solid:liquid ratio (**Table 1**). Colorimetric assays and liquid chromatography (HPLC-PDA-MS/MS) analyses were performed to characterize the extracts according to phenolic composition and radical scavenging capacities.

Optimal conditions were stablished for extraction of 20 min using ethanol at 40% and a ratio of 1:30 (w:v). The extract provided high antioxidant activity, reaching an EC_{50} over 90 mg/L. Several polyphenols were identified by MS/MS liquid chromatography and the main ones were quantified by PDA through external standards curves.

Date by-products supplied antioxidant compounds with the potential to be used in the food industry, reducing agroindustrial waste. UAE applying ethanolic solutions has demonstrated to be an alternative to organic solvents and high-consume energy extractions.

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Valorização de biorresíduos da produção de sumo de laranja: extração de ácido cítrico

Filipa A. Fernandes[1,2,3], **José Pinela**[1,2], **Márcio Carocho**[1,2], **Miguel A. Prieto**[3], **Sandrina A. Heleno**[1,2,*], **Lillian Barros**[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3]Grupo de Nutrición y Bromatología, Departamento de Química Analítica y Alimentaria, Facultad de Ciencias de Ourense, Universidad de Vigo-Ourense Campus, E-32004 Ourense, Spain

**sheleno@ipb.pt*

A laranja é um dos frutos mais consumidos mundialmente, sendo uma parcela considerável destinada à produção de sumos, operação industrial que gera uma grande quantidade de resíduos (polpa, cascas e sementes). Uma parte destes biorresíduos é utilizada na produção de ração animal; contudo, uma quantidade significativa ainda é depositada em aterros sanitários, gerando um impacto ambiental considerável [1,2,3]. As atividades biológicas da casca de laranja, como os potenciais antimicrobianos e antioxidantes foram já comprovados por diversos estudos; no entanto, são escassos os trabalhos sobre técnicas de extração eficientes para obtenção de compostos bioativos a partir destes subprodutos [4]. Assim, o principal objetivo deste trabalho foi a valorização das cascas de laranja, promovendo a sua reciclagem em ingredientes naturais, com recurso à otimização de técnicas de extração para obtenção de extratos ricos em ácido cítrico (agente antimicrobiano, acidificante e aromatizante). Para isso, foi selecionada a técnica de extração assistida por ultrassons, aplicando um delineamento experimental consistindo num desenho central composto rotativo usando a metodologia de superfície de resposta para otimização, o qual combinou cinco níveis das variáveis independentes: percentagem de etanol (0-100%), tempo (2-45 min) e intensidade ultrassónica (50-500 W). Os teores de ácido cítrico foram determinados por UFLC-PDA e usados como resposta da otimização. O software Design-Expert foi usado para modelação e análise gráfica dos dados. Os modelos teóricos desenvolvidos foram ajustados com sucesso aos dados experimentais, validados estatisticamente com base em altos valores de F e R^2 e usados para prever as condições ótimas que maximizam a recuperação de ácido cítrico a partir da casca de laranja. Utilizando as condições ideais de processamento obtidas, nomeadamente intensidade ultrassónica média (119,2 W), tempo de extração médio (35,5 min.) e proporção de etanol baixa (0 %, *v/v*), foi prevista a recuperação de 6,4 g de ácido cítrico por 100 g de casca de laranja desidratada. A extração assistida por ultrassons revelou-se uma técnica promissora para a obtenção de ácido cítrico a partir destes biorresíduos de laranja, tornando possível a sua valorização através da obtenção de moléculas de elevado valor acrescentado com potencial aplicação em várias indústrias, como a alimentar.

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Collagen determination in fish skin: development of a flow analysis system for quantification of hydroxyproline

Maria M. P. Melo, Ezequiel R. Coscueta, Manuela E. Pintado, Raquel B. R. Mesquita, António O. S. S. Rangel*

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327 4169-005, Porto, Portugal
arangel@ucp.pt

Collagen is a protein with various applications, namely in the food area. It has valuable properties, since it is a polymer with weak antigenicity, low toxicity, and high nutritional value, among other features [1]. Its extraction from mammalian sources, i.e., bovines, is decreasing due to health and environmental problems and, therefore, fish have become a good alternative for collagen resources [2].

One way to quantify the collagen present in fish skin, in order to obtain high-value fractions, is the determination of hydroxyproline (HYP), an amino acid highly present in collagen [1]. The determination of HYP from fish skin requires the hydrolysis of a skin section, to break collagen in its amino acids and the HYP value quantified is compared to the amount present in pure collagen, studied previously (38 µg of HYP per mg of pure collagen).

The quantification of HYP is based on its oxidation combined with the reaction with DAB (dimethylaminobenzaldehyde) that forms a chromophore-coloured product. The HYP can then be correlated with the spectrophotometric measurement of this coloured product. A batchwise approach was performed to study the best reaction conditions, namely different reagents, heating times and proportions.

The main goal of this work is to develop an automated flow injection analysis (FIA) method, to miniaturize the determination of HYP. Several operation parameters like flow rates, number of channels, tube diameters and lengths of reactors will be studied to optimize the developed FIA method.

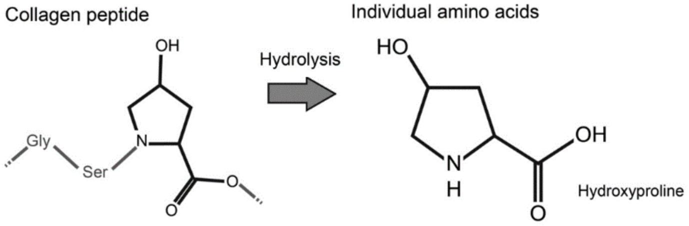

Fig.1. Scheme of collagen break into hydroxyproline, through a hydrolysis process; adapted from Cissel et al [3].

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ALM43

Phlorotannins-rich extract from *Laminaria digitata* for the development of a functional granola towards prevention of Diabetes mellitus

Marcelo D. Catarino[1,*], Marionela Covic[1], Artur M. S. Silva[1], Susana M. Cardoso[1]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
**mcatarino@ua.pt*

Diabetes mellitus is a chronic disease that leads to a degenerative and debilitating condition in the patient's quality of life. Prevention is the best way to fight this disease through healthy eating habits. Macroalgae has been reported as a rich source of bioactive compounds, namely phlorotannins with beneficial effects in the prevention of diabetes and a great potential for the application in new functional foods [1]. The aim of this work is the development of a functional granola, enriched with a phlorotannins-rich extract from the brown macroalgae *Laminaria digitata*. The UHPLC-ESI-MS analysis at 280 nm revealed a chromatographic profile characteristic of phlorotannins, showing an unresolved hump typical of unseparated higher molecular weight compounds preceded of small peaks corresponding to oligomeric phlorotannins (fig.1). The antioxidant activity measured by the $NO^{\bullet}$ and $O_2^{\bullet-}$ scavenging methods and the inhibitory effect on α-amylase and α-glucosidase was also evaluated. Interestingly, the inhibition activity against α-amylase was similar to acarbose and against α-glucosidase was approximately 200-fold higher than acarbose and 3-fold higher than other phlorotannin-rich extracts from *Fucus vesiculosus* [2]. Adding this this phlorotannins-rich extract to granola (2%) got a good acceptance in the sensory analysis and contributed to the inhibition of both enzymes, especially α-glucosidase. This work shows that the phlorotannin-rich extracts of *Laminaria digitata* have great potential to be used as an ingredient for the development of functional foods that can help prevent diabetes.

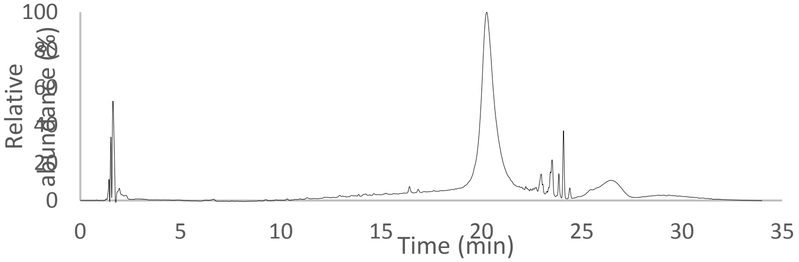

Figure 6. Chromatographic profile of Laminaria digitata ethanol extract at 280 nm.

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Multiple mycotoxin analysis method for rice

Sousa Monteiro, C.[1,*], Faria, MA.[1], Pinto, E.[2,3], Cunha, S.[1]

[1]LAQV-REQUIMTE, Laboratory of Bromatology and Hydrology, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Laboratory of Microbiology, Biological Sciences Department, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3]Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Matosinhos, Portugal
*carolinasousamonteiro@gmail.com

Rice is an essential grain crop and one of the most important for almost half of the world's population [1]. Fungi may affect rice during all food chain supply, in the field, and post-harvesting, and they are responsible for significant yield losses and economic burden. Mycotoxins occurrence in food products is unpredictable and unavoidable worldwide, and according to Rapid Alert System for Food and Feed, the main hazard cited in EU border rejection notifications [2,3]. Here we propose an HPLC-MS/MS method for the analysis for 22 mycotoxins (13 regulated and 9 emergent) and their evaluation in 17 rice market samples.

Mycotoxin extraction was performed according to a QuEChERS procedure with some modifications (described in the poster) [4]. MS/MS analysis was performed on a Quattro Premier XE (Waters) mass spectrometer interfaced with the high-performance liquid chromatography (HPLC) system Waters ACQUITY. A ACQUITY UPLC BEH C18 1.7 µm particle size analytical column (100 × 2.1 mm) was used for chromatographic separation. Gradient elution was performed using a mobile phase constituted by a phase A (water/methanol/acetic acid, 94:5:1 (v/v) and 5 mM ammonium acetate) and a phase B (methanol/water, 98:2 (v/v) and 5 mM ammonium acetate).

Most of the samples (11/17) were contaminated with more than one mycotoxin. Eleven out of 22 mycotoxins under study were found in the analyzed samples. Overall, aflatoxin B1 was the most frequently detected, followed by zearalenone. In addition, other toxins, such as 3-acetyldeoxynivalenol, HT-2 toxin, aflatoxin B2, 15-acetyldeoxynivalenol, aflatoxin G1, T-2 toxin, sterigmatocystin, beauvericin, cyclopiazonic acid were present in some of the samples.

These results contribute to the increased knowledge of mycotoxin contents in cereals marked in Portugal, and they highlight the deep need to further studies to overcome the absence of legislated limits for emergent mycotoxins.

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Promising bioactive properties from *Moringa oleifera* seed cake protein hydrolysates

Zita E. Martins[1,*], Tânia Tavares[2,3], Susana Pinho[1], Miguel A. Faria[1], Isabel M.P.L.V.O. Ferreira[1]

[1]LAQV/REQUIMTE, Laboratory of Bromatology and Hydrology, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, 4050-313, Portugal
[2]LEPABE—Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, Porto, 4200-465, Portugal
[3]ALiCE—Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal
**zmartins@ff.up.pt*

Moringa oleifera seed cake, a by-product of Moringa oil extraction, is an interesting source of protein with bioactive properties that has promising health benefits [1]. The goal of this work was to optimize the production of protein hydrolysates from Moringa Oleifera seed cake by enzymatic extraction with alcalase from *Bacillus licheniformis* and evaluate its bioactivity (antioxidant, ACE-inhibition, cellular ROS-inhibition and cytotoxicity).

Optimum conditions were determined by surface response, where reaction time and enzyme/substrate ratio were used as parameters and degree of hydrolysis (DH), angiotensin I converting enzyme-inhibitory (ACE) activity and antioxidant activity were used as objective functions. The suggested model showed to be statistically suitable to describe DH, ACE-inhibitory activity and antioxidant activity of hydrolysates. Cytotoxicity as evaluated by the MTT assay in human Caco-2 cells differentiated for 7 day after 24 h exposure. ROS production was assessed after 24 h pre-exposure to samples before 10 µM DCFH-DA incubation for 30 min before ROS induction by 2.5 mM H_2O_2.

The optimum conditions observed for alcalase was: 5.8 h, 2.1 %(v/v). For optimum conditions hydrolysates presented ACE-inhibitory activity characterized by an IC50 of 42.6 ± 2.0 and 25.7 ± 3.0 µg/mL, for the total and <3 kDa fractions, respectively. For antioxidant activities, results obtained through the ORAC method for total and <3 kDa fractions were 2.60 ± 0.04 $\mu mol_{Trolox\ equivalent}/mg_{hydrolysed\ protein}$ and 1.96 ± 0.06 $\mu mol_{Trolox\ equivalent}/mg_{hydrolysed\ protein}$, respectively. Concerning cytotoxicity in Caco-2 intestinal cells total hydrolysates reduced cell viability to 87% at 5 mg/mL whilst cytotoxic effects were noticed for <3 kDa fractions at 7.5 mg/mL. ROS production after 2.5 mM H2O2 treatment was significantly reduced by total hydrolysate at 0.25 and 1 mg/mL and from 0.1 mg/mL by <3 kDa fractions. The <3 kDa fractions presented thus the highest activity across all the assays performed.

This study showed the great potential of Moringa seed-cake extract to yield bioactive peptides with promising bioactivity which can play a role in the reduction of cardiovascular diseases, being suitable for use as a functional ingredient in nutraceutical and pharmaceutical applications.

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Evaluation of phenolic compounds present in prunings of native Galician olive trees

P. Reboredo-Rodríguez[1*], S. Rivas[2], A. Moure[2], H. Domínguez[2], M. Figueiredo-González[1], C. González-Barreiro[1], B. Cancho-Grande[1]

[1] Food and Health Omics, Department of Analytical and Food Chemistry, Faculty of Science, University of Vigo – Ourense Campus, 32004 Ourense, Spain
[2] Chemical Engineering Department, University of Vigo (Campus Ourense), Faculty of Sciences, Polytechnical Building, As Lagoas 32004 Ourense, Spain
**preboredo@uvigo.es*

Although the main olive growing areas in Spain are in Andalusia, new regions have emerged in recent years that are devoted to the cultivation of this vegetable oil and to the exploitation of native varieties (Brava Gallega and Mansa de Figueiredo) and/or foreign ones (Arbequina and Picual) to produce high quality virgin olive oil. This is the case of the oils produced in Galicia, where olive trees have become an alternative crop, probably due to climate change in recent decades, among other factors [1].

The olive oil sector generates a large amount of by-products or wastes, due to pruning practices, harvesting, olive grinding, etc. The wastes generated by the pruning practices, which are burned or left in the fields as compost, represent an environmental problem and an added management task for the farmer, and these have not been studied yet. Recent research, however, focused on the recovery of by-products and wastes generated by the olive oil industry, have shown a high content in molecules of high added value such as phenolic compounds, which constitute a huge resource of bioactive molecules [2,3]. Therefore, it is essential to know the composition of the by-products or waste generated to better define appropriate processes that allow the recovery of substances of high added value with beneficial health properties [4].

The objective of this research was an assessment of the phenolic compounds present in the pruning of the native Galician varieties of olive trees Brava Gallega and Mansa de Figueiredo. To achieve this objective, a solid-liquid extraction was performed with ethanol:water (90:10, v/v) followed by the determination of the total phenolic compounds and the antioxidant capacity using spectrophotometric methods. After that, the main phenolic compounds were characterized by HPLC-DAD. A total of 12 phenolic compounds were determined, and the majority of them were oleuropein, luteolin-7-*O*-glucoside and taxifolin. These phenolic compounds can be used in the food, cosmetic or pharmaceutical industries since they present beneficial properties for health (antioxidants, antimicrobials, anticancer or antidiabetic, among others).

This is a first step towards promoting a sustainable bioeconomy in the province of Ourense taking advantage of the emerging cultivation of olive trees.

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Bioaccessibility of phenolic compounds from Galician olive leaf infusions

P. Reboredo-Rodríguez*, G. Leuyacc-del Carpio, F. López-Varela, C. González-Barreiro, B. Cancho-Grande, M. Figueiredo-González

Food and Health Omics, Department of Analytical and Food Chemistry, Faculty of Science, University of Vigo - Ourense Campus, 32004 Ourense, Spain
**preboredo@uvigo.es*

Olive leaf, one of the most abundant by-products of olive tree production, is a source of extracts rich in phenolic compounds with potential health benefits [1]. The traditional use of "olive leaf infusions" in folk medicine to combat intestinal diseases, hypertension, fevers and other diseases, such as malaria [2], has been related to their phenolic composition. However, the biological effects of olive leaf phenolics are conditioned by their bioaccessibility, defined as, the amount of phenolic compounds extracted from the olive leaf matrix that might be able to pass through the intestinal barrier.

Taking this into account, the objective of this work is to evaluate the phenolic compounds and antioxidant activity of olive leaf infusions of the native Galician olive trees before and after a gastro-intestinal process. The determination of the total phenolic compounds and the antioxidant activity of infusions were performed by conventional spectrophotometric methods. Moreover, the main phenolic compounds were quantified by HPLC-DAD. To predict their bioaccessibility, the INFOGEST protocol has been followed. This procedure is an *in vitro* static method which simulate the gastro-intestinal digestion [3].

The olive leaf infusions present high phenolic concentration with oleuropein, luteolin-7-*O*-glucoside, verbascoside and rutin being among the ones with higher value, as well as high antioxidant activity. The total phenolic amount and antioxidant activity of the infusions after the digestion process showed lower values than those registered before the *in vitro* digestion. However, high bioaccesibility for some phenolic compounds was found.

Therefore, the high phenolic compounds from olive leaf infusions after digestion shows their potential to be used in the future in pharmaceutical and/or nutraceutical industries.

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Caracterização química de uma massa alimentícia com bagaço de azeitona

Joana C. Lobo, Bárbara Oliveira, Diana Melo Ferreira, Anabela S. G. Costa, Rita C. Alves, M. Beatriz Oliveira*

REQUIMTE/LAQV, Faculty of Pharmacy of the University of Porto, Porto, Portugal
**beatoliv@ff.up*

A procura por produtos saudáveis e funcionais tem crescido nos últimos anos. A tecnologia alimentar tem-se desenvolvido nesse sentido de forma a responder às necessidades dos consumidores, que são cada vez mais exigentes e conscientes das suas escolhas alimentares.

O bagaço de azeitona (BA) é um subproduto da produção do azeite cujo impacto ambiental é uma preocupação, mas que simultaneamente é uma fonte de fibra, proteína, ácidos gordos e outros compostos bioativos [1] que lhe conferem potencial como ingrediente alimentar.

O objetivo deste trabalho foi a caracterizar quimicamente uma massa alimentícia enriquecida com 7,5% de BA e proceder à sua comparação com uma massa controlo (MC) que continha apenas farinha de trigo.

A caracterização nutricional das massas foi avaliada por métodos oficiais AOAC [2] e o teor de hidratos de carbono foi calculado por diferença. Foi também caracterizado o perfil lipídico através da determinação dos perfis de ácidos gordos (GC-FID) [2] e da vitamina E (HPLC-DAD-FLD) [2].

De acordo com os resultados obtidos, verifica-se que a incorporação de BA na massa levou ao aumento do teor total de minerais, gordura, fibra total, insolúvel e solúvel, e vitamina E, comparativamente com a MC.

Pode-se então concluir que a incorporação do subproduto BA tem vantagens na valorização nutricional de massas alimentícias. Parece ser um ingrediente com interesse para a esta indústria, indo ao encontro das necessidades atuais dos consumidores.

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Pasta de bagaço de azeitona: ingrediente promissor para a indústria cosmética e alimentar?

Joana C. Lobo[1], Diana Melo Ferreira[1], Susana Machado[1,2], Anabela S. G. Costa[1,2], Rita C. Alves[1], M. Beatriz P.P. Oliveira[1*]

[1]REQUIMTE/LAQV, Faculty of Pharmacy of the University of Porto, Porto, Portugal
[2]Grupo de Bromatologia e Nutrição, Departamento de Química Analítica e Ciência Alimentar, Faculdade de Ciências, Universidade de Vigo, Ourense, Espanha
**beatoliv@ff.up.pt*

A obtenção de azeite é acompanhada pela produção de subprodutos, cuja acumulação pode acarretar problemas ambientais. No entanto, alguns compostos presentes nestes subprodutos, nomeadamente no bagaço de azeitona (BA), têm atividade antioxidante e valor nutricional interessantes. O conhecimento da sua composição permite inferir o seu potencial como ingrediente para a indústria alimentar e cosmética [1].
Este estudo teve como objetivo avaliar a composição química da pasta de bagaço de azeitona (PBA), obtida por compressão do BA fresco e centrifugação da semipasta resultante. Após a remoção do sobrenadante, a PBA foi liofilizada e analisada.
Foram determinados os teores de gordura, proteína, cinzas e fibra total (métodos AOAC) [2] e os hidratos de carbono obtidos por diferença; perfil de ácidos gordos (GC-FID); perfil de vitamina E (HPLC-DAD-FLD); e teor de hidroxitirosol (HPLC-DAD-FLD) [1]. Foram ainda analisados os teores de compostos fenólicos totais e a atividade antioxidante (pelos métodos FRAP e inibição do DPPH$^•$) [3]. Os resultados foram expressos em peso seco.
A PBA continha teores elevados de fibra total (48,5%) e hidratos de carbono disponíveis (31,1%), além de teores consideráveis de proteína (8,5%), gordura (7,7%) e minerais totais (4,2%). O ácido oleico apresentou-se como o ácido gordo maioritário; o teor total de vitamina E foi de aproximadamente 45 mg/kg, sendo identificados três vitâmeros (α-, maioritário, β- e γ-tocoferol). O teor de hidroxitirosol foi de 6,1 mg/g. O PBA apresentou, ainda, um teor em compostos fenólicos totais de 33,7 mg de eq. ácido gálhico/g. No que diz respeito à atividade antioxidante, os valores obtidos pelos métodos FRAP e inibição do DPPH$^•$ foram de 67,9 mg de eq. sulfato ferroso/g e 49,5 mg de eq. trolox/g, respetivamente.
A PBA mostra potencial para diferentes aplicações, respondendo às questões de sustentabilidade ambiental e diversificação de produtos no mercado. A presença de antioxidantes e nutrientes permite pensar em aplicações para as indústrias cosmética e alimentar.

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RELIABLE IN-LINE DETERMINATION OF THE PROTEIN, FAT, SODIUM AND SALT CONTENT IN PASTY DOUGHS THROUGH NEAR INFRARED SPECTROSCOPY AND CHEMOMETRICS

D. Castro[1,2,*], M.C. Ortiz[1], S. Sanllorente[1], L.A. Sarabia[3], J.M. Amigo[4,5], I. García[2]

[1]Departamento de Química, Facultad de Ciencias, Universidad de Burgos; Plaza Misael Bañuelos s/n, Burgos 09001, Spain
[2]AOTECH (Advanced Optical Technologies S.L.), Escuela Ing. De Bilbao; Plaza Ingeniero Torres Quevedo, 1 2º, 48013, Bilbao, Spain
[3]Departamento de Matemáticas y computación, Facultad de Ciencias, Universidad de Burgos; Plaza Misael Bañuelos s/n, Burgos 09001, Spain
[4]IKERBASQUE, Basque Foundation of Science, Plaza Euskadi 5, 48009 Bilbao, Spain
[5]Dept. Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU). Barrio Sarriena s/n. 48940 Leioa, Spain
**dcr1002@alu.ubu.es*

Near Infrared spectroscopy (NIR) is an attractive technique in the food industry, where new and more reliable methods for evaluating the quality of the final products are continuously demanded. One of the main advantages of NIR spectroscopy is the capability to register a large amount of spectral information in a short time. If used on the production line itself, it enables non-destructive measurements with no sample preparation, allowing the determination of multiple parameters simultaneously. In this way, continuous monitoring of production quality is achieved, verifying the attributes of raw materials and the specifications of the final product, increasing its quality with stricter control.

To extract the relevant information from NIR spectra in food, several chemometric methods, like Partial Least Squares Regression, have been demonstrated to be powerful tools [1,2]. In this context, we study the potential usefulness of the AONIR in-line measuring platform developed by AOTECH [3]. To do that, it was measured the reflectance in a wavelength range between 900 and 1670 nm. When analyzed with Partial Least Squares, quantitative information of the protein, fat, sodium, and salt content in pasty doughs manufactured in Hornos de Lamastelle [4] is obtained. Due to the characteristics of the in-line setup, some variability was observed in the spectra depending on the area of the dough in which the measurements were taken. For that reason, an additional study was also carried out to reduce the variability concluding that the most stable measurement was in the center of the doughs.

The resulting models presented an R^2 CV between 0.906 and 0.971, and a root mean square error in cross-validation (RMSECV) between 0.076 and 0.379 % (Table 1), allowing the rapid and efficient determination of the parameters studied.

Table 1. R^2C, R^2 CV, RMSEC and RMSECV of protein, fat, sodium and salt models

Arial	R^2C	R^2 CV	RMSEC (%)	RMSECV (%)
Protein	0.980	0.953	0.065	0.102
Fat	0.934	0.906	0.317	0.379
Sodium	0.977	0.968	0.065	0.076
Salt	0.983	0.971	0.137	0.180

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IN-LINE APLICATION OF NEAR INFRARED SPECTROSCOPY FOR THE CLASSIFICATION OF DOUGHS IN BAKERY

D. Castro[1,2,*], M.C. Ortiz[1], S. Sanllorente[1], L.A. Sarabia[3], J.M. Amigo[4,5], I. García[2]

[1]Departamento de Química, Facultad de Ciencias, Universidad de Burgos; Plaza Misael Bañuelos s/n, Burgos 09001, Spain
[2]AOTECH (Advanced Optical Technologies S.L.), Escuela Ing. De Bilbao; Plaza Ingeniero Torres Quevedo, 1 2º, 48013, Bilbao, Spain
[3]Departamento de Matemáticas y computación, Facultad de Ciencias, Universidad de Burgos; Plaza Misael Bañuelos s/n, Burgos 09001, Spain
[4]IKERBASQUE, Basque Foundation of Science, Plaza Euskadi 5, 48009 Bilbao, Spain
[5]Dept. Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU). Barrio Sarriena s/n. 48940 Leioa, Spain
**dcr1002@alu.ubu.es*

Near-infrared spectroscopy (NIR) has demonstrated to be a very powerful technique in the food industry to assess the quality of raw materials and the final product. The use of NIR spectroscopy to determine certain quality parameters through partial least squares-discriminant analysis (PLS-DA) is quite widespread in the industry [1]. This is possible thanks to the fact that this instrumental technique allows recording rich and fast spectral information quickly, carrying out a non-destructive analysis without sample preparation.

In this work, the ability of the AONIR in-line measuring platform developed by AOTECH [2] has been demonstrated to detect deficiencies in the dough kneading process. Also, the possibility of differentiating between correctly and not correctly kneaded doughs, has been verified through the rolling process. To do this, both processes have been monitored by measuring the reflectance in a wavelength range between 900 and 1670 nm. To study deficiencies in the kneading process, a principal component analysis has been carried out with the analyzed doughs. On the other hand, to differentiate between correctly kneaded doughs and those that are not, a sequential decision-making procedure has been used to differentiate first, between correct and incorrect doughs; secondly, within the incorrect doughs, differentiate between those with problems with the kneading time and those that have problems with the amount of water; and lastly, within the latter, differentiate between those that have an excess of water or a deficit of water. In this way, a total of three PLS-DA (Partial Least Squares Discriminant Analysis) models have been built. Every analysis has been accomplished by coupling the AONIR to the industrial process in the company Daveiga [3].

In the case of the kneading process, a total of 1235 samples have been analyzed, recording their spectrum at 125 different wavelengths. With the analysis of the first two principal components, which explain a 90 % of the variance, it has been concluded that an excess of water does not suppose a serious problem in the kneading process, while a deficit, or a short time of kneading, does. Whereas, for the rolling process, the resulting classification models needed only two latent variables, and a classification success rate of 100 %.

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Amino acid profile: comparison among coffee silverskin and green and roasted beans

Susana Machado[1,2], Marlene Machado[1], M. Beatriz P.P. Oliveira[1], Jesus Simal-Gandara[2], Rita C. Alves[1]*

[1]REQUIMTE/LAQV, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Universidade de Vigo, Nutrition and Bromatology Group, Analytical Chemistry and Food Science Department, Faculty of Science, E32004 Ourense, Spain
**rcalves@ff.up.pt*

Coffee is a popular beverage consumed mainly for its stimulating properties. *Coffea arabica* L. and *Coffea canephora* Pierre ex A. Froehner (also known as robusta) are the more important varieties at economical level. Nowadays, there are an increased interest in coffee bioactives from green and roasted beans, as well as from by-products. To obtain roasted coffee, several processing steps are needed with generation of different by-products. Silverskin remains on the green beans after cherries processing [1], being released during roast (major by-product from coffee roasting industries). In this research, the amino acid profile of coffee silverskin, green coffee and roasted coffee beans was analysed and compared.

Green beans from arabica coffee produced in Brazil were kindly provided by a Portuguese coffee company. One part of the beans was roasted (~210 °C, 10 min) and, then, roasted beans and silverskin were collected separately. The samples were stored at room temperature, in a dry place, and protected from light. For analysis, the samples were ground and homogenized. Alkaline (4 M KOH, 110 ºC, 4h) and acid (6 M HCl, 110 ºC, 24 h) hydrolyses were performed to obtain tryptophan and the remaining amino acids, respectively. The hydrolysates were neutralized and submitted to automatic pre-column online derivatization with OPA/3-MPA and FMOC, followed by RP-HPLC-FLD analysis [2]. The amino acids were identified by comparing their retention times with those of standards. Quantification was performed through the internal standard method, using norvaline as internal standard. The results were expressed in dry weight.

The amounts of total amino acids were 83.18, 108.60, and 80.14 mg/g, for silverskin, green coffee and roasted coffee beans, respectively. The major individual amino acids were glutamic acid, aspartic acid and leucine (21.76, 11.97 and 8.55 mg/g, respectively) for the green beans; glutamic acid, leucine and aspartic acid (19.96, 8.40, and 8.07 mg/g, respectively) for roasted beans; and aspartic acid, glutamic acid and leucine (11.04, 9.31, and 6.67 mg/g, correspondingly) for silverskin. The important branched-chain amino acids (valine, isoleucine and leucine) are also present in substantial amounts (4.64-5.18, 4.14-5.04 and 6.67-8.55 mg/g, respectively) in all samples. Although in low amount, methionine (0.74 mg/g for silverskin) and hydroxyproline (0.41 and 0.45 mg/g, for roasted beans and green beans, respectively) were also identified.

The essential amino acids present in silverskin is almost similar to roasted coffee (32.10 and 32.38 mg/g, respectively). For green coffee this value was higher, 40.94 mg/g. In fact, roasted beans and silverskin are roasted at high temperatures, with an expected degradation of amino acids by participation in Maillard reactions. The similarity of silverskin amino acid profile with roasted coffee highlights its potential as a source of important amino acids in new formulations.

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Comparison of the amino acid profile of two by-products of the coffee industry: pulp and husk

Marlene Machado[1,*], Susana Machado[1,2], Helena Ferreira[3], M. Beatriz P. P. Oliveira[1], Rita C. Alves[1]

[1]REQUIMTE/LAQV, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, University of Vigo, Ourense, Spain
[3]REQUIMTE/UCIBIO, Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Portugal
**marlenemachado753@gmail.com*

The transformation of coffee cherries into roasted beans produces a variety of chemically interesting by-products. Dehulling the cherry allows obtaining the by-products coffee pulp and coffee husk, depending on the method used, wet or dry, respectively [1]. Previous studies on coffee pulp or coffee husk have focused mainly on the profile of phenolic compounds and their antioxidant activity [1,2,3]. Important amino acids are also present in these by-products [2], however, studies on their profile in coffee pulp and husk are still limited [2]. The amino acid composition is essential to estimate not only the real protein content, but also the protein quality of coffee husk and pulp [4]. Thus, the aim of this study was to compare the amino acid profile of two coffee by-products: coffee pulp (*Coffea arabica*, from Colombia) and coffee husks (*Coffea canephora*, from Panama). Dried samples were kindly provided by Colombian and Panamanian producers through a national coffee importer and roaster company (JMV-José Maria Vieira, SA).

For tryptophan quantification, samples were hydrolyzed under alkaline conditions (4 M KOH, 110 °C, 4h). For the remaining amino acids, acid hydrolysis (6 M HCl, 110 °C, 24h) was performed. Analyses were performed in triplicate. The hydrolysates were neutralized, submitted to an automated online derivatization with OPA and FMOC and analyzed by RP-HPLC/FLD. Amino acids were identified by comparing their retention times with those of known standards and quantified by the internal standard method using calibration curves obtained for each compound [4].

The results show that coffee by-products contain a variety of essential and non-essential amino acids. Except for aspartic acid, all the amino acids were significantly higher ($p<0.05$) in the coffee pulp. Leucine was the main essential amino acid determined (4.08 ± 0.26 and 2.35 ± 0.11 mg/g dry weight [dw] for pulp and husks, respectively). Regarding non-essential amino acids, aspartic acid predominated (6.63 ± 0.44 and 7.50 ± 0.56 mg/g dw for pulp and husks, respectively). The sum of total amino acid (∑TAA) refers to the true protein content of by-products. Coffee pulp (50.35 ± 2.91 mg/g dw) showed a significantly higher ($p<0.05$) ∑TAA compared to coffee husks (35.64 ± 1.56 mg/g dw).

In conclusion, both by-products could be a potential source of essential and non-essential amino acids. The consumption of coffee pulp and husk should be promoted due to the richness in bioactive compounds, but also to answer the circular economy and sustainability issues.

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Maltodextrin Microencapsulation of Phenolic-rich Fractions of *Gunnera tinctoria* Extracts

Faezeh Fathi, Reza M. Kouchaksaree, Rita C. Alves, M. Beatriz P. P. Oliveira

[1]REQUIMTE/LAQV, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal.
*ffathi@ff.up.pt

Gunnera tinctoria (Nalca or giant rhubarb) is a flowering plant native to South America and classified as invasive in South Europe. It is a source of phenolic compounds (gallic acid, ellagic acid, catechin, epicatechin, and quercetin) with reported antioxidant and antitumoral activities [2]. In fact, phenolic compounds are secondary metabolites responsible for numerous plant biological, physiological, and chemical activities. However, their low bioavailability and high structural sensitivity limit *in vivo* functionalities [1].

Encapsulation by natural polymers should be a practical, safe, and green strategy to protect sensitive bioactive compounds against environmental hazards, storage conditions, industrial processes, and biologic media (controlled release), such as temperature, light, pH, water, oxygen level and digestive system. Having this in view, encapsulation of natural products have been widely developed as efficient delivery carriers for food, cosmetic and pharmaceutical applications [1,2].

Maltodextrin, a hydrolyzed starch, is an example of an efficient encapsulation agent due to its high water solubility, low viscosity, emulsification improver, high protection, and ability to provide a controlled release.

In this study, a phenolic-rich fraction of *G. tinctoria* extract was obtained by adsorbent resin column chromatography (Relite EXA90) and subsequently encapsulated by spray-drying using maltodextrin as protective agent [1]. Product yield, particle size (regarding internal and external layers), surface charges, and surface morphology (by scanning electron microscopy, SEM) were determined in encapsulated particles.

The total phenolic content increased almost 2.23-fold compared with the crude extract. The phenolic-rich fraction loaded into maltodextrin presented a product yield of 46%. The mean particle size was 397.9 nm (volume) and 327.1 nm (number), concerning internal layers, and 1-20 µm regarding the external layer, values confirmed by DLS and SEM images, respectively. The surface charge was −33.82 ± 0.76 mV in the internal layer and −31.40 ± 10.29 mV in the external layers, all in an acceptable and stable range. The layers were orientated based on Type A-II and Type A-III schematic formation [2].

The maltodextrin encapsulated phenolic-rich extract proved to be a suitable carrier for antioxidants delivery concerning the physiochemical properties of the formulated particles and the green and safe methodology used.

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Occurrence of Coccidiostats in Portuguese Eggs

Rui R. Martins [1,2], Liliana J.G. Silva [1,] , André M. P. T. Pereira [1], Alexandra Esteves [2], Sofia C. Duarte [1,3], Andreia Freitas [4,5], and Angelina Pena [1*]

1 LAQV, REQUIMTE, Laboratory of Bromatology and Pharmacognosy, Faculty of Pharmacy,
University of Coimbra, Polo III, Azinhaga de Sta Comba, 3000-548 Coimbra, Portugal
2 Animal Research Centre (CECAV), University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
3 Centro de Investigação Vasco da Gama, Escola Universitária Vasco da Gama (EUVG), Av. José R. Sousa Fernandes 197, Campus Universitário de Lordemão, 3020-210 Coimbra Portugal
4 National Institute for Agricultural and Veterinary Research (INIAV), I.P., Av. da República, 2780-157 Oeiras, Portugal
5 Associated Laboratory for Green Chemistry of the Network of Chemistry and Technology, REQUIMTE/LAQV, R. D. Manuel II, Apartado 55142, 4051-401 Porto, Portugal
* Correspondence: *apena@ff.uc.pt*; Tel.: +35-1239488400; Fax: +35-123982712

Since 2000, egg consumption has increased sharply (by about 50%) according to reports from the Food and Agriculture Organization. A continuous increase in demand for hen eggs and their products is expected, due to their widespread consumer acceptance, an increase in individual consumption, and an increase in population[1].

In today's world, food of animal origin cannot be produced without the use of veterinary medicines and feed additives[2]. As a result of intensive broiler production, coccidiostats are prophylactically administered in feed to prevent a costly outbreak of coccidiosis, consequently coccidiostat residues may be retained in eggs. These products, when consumed in significant quantities, may pose a health risk to humans, cause pathophysiological effects, drug resistance and allergies, poisoning, carcinogenicity, and teratogenicity [3].

Taking into-account the European legislation, the main goal of this work was to evaluate the presence of nine coccidiostats (lasalocid, maduramicin, monensin, narasin, robenidine, salinomycin, halofuginone, diclazuril and nicarbazin) in Portuguese produced and commercialized eggs by HPLC-MS/MS method.

The method was successfully validated, according to Decision 2002/657/EC, and applied to the detection of coccidiostats in 63 egg samples. Sampling was carried out in the north and center of mainland Portugal, with 29 corresponding to home produced eggs and 35 commercially acquired eggs from supermarkets.

The synthetic coccidiostat found was diclazuril with a detection frequency of 4.76% (n=3), all positive samples corresponding to homemade samples with maximum concentration of 33.92 µg kg-1, and a total average of 2.353 µg kg-1. In the analyzed samples, ionophore coccidiostats presented the highest contamination frequencies, namely nicarbazin, that showed values of 85.7% (n=54). Maximum and mean values were 124.1 µg kg-1, and 45.18 µg kg-1 in homemade samples and in supermarket samples the values were 37.07 µg kg-1 and 28.40 µg kg-1, respectively.

Nicarbazin and diclazuril, were found together in two homemade samples (3.17%).

The occurrence of coccidiostat residues in eggs, besides the improper treatment of laying hens may be related to feed production, due to the so-called "carry over" effect during the production of medicated feeds. However, given the scarcity of published studies on this topic and the fact that the Portuguese National Plan for Residue Research did not include the analysis of samples of either eggs or birds, it is imperative to draw more attention to this issue, namely by widening the number and type of foodstuffs sampled.

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Antitumoral Activity of *Gunnera tinctoria* Extracts on a Pancreatic cell line

Faezeh Fathi[1*], Anabela S. G. Costa [1,2], Nelson Andrade[1], Cláudia Silva[3], Fátima Martel[3], Rita C. Alves[1], M. Beatriz P. P. Oliveira[1]

[1]REQUIMTE/LAQV, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal.
[2]Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, University of Vigo, Ourense, Spain
[3]Unit of Biochemistry, Department of Biomedicine, Faculty of Medicine of Porto, University of Porto, Portugal
*ffathi@ff.up.pt

Gunnera tinctoria (Nalca) belongs to the Gunneracea family, and is used for culinary purposes in South America. In Azores, Portugal, this plant is considered as invasive [1]. *G. tinctoria* is widely known for its antioxidant activity due to the high content of phenolic compounds, namely gallic acid, ellagic acid, catechin, epicatechin, and quercetin [2].

Relite EXA90 (adsorbent resin column chromatography) was used to enrich the phenolic content of *G. tinctoria* extracts to improve the extract's bioactivity. The extracts were obtained from maceration of adult leaves (freeze-dried and ground) with mixtures of ethanol: water (100:0, 50:50, 30:70, and 0:100; 2 L each), in triplicate. The extracts were combined, and ethanol eliminated by a rotary evaporator. Afterwards, the concentrated extract was subjected to Relite EXA90 resin column. The phenolic compounds were adsorbed on the resin surface, and non-active compounds eliminated. Then, they were desorbed with ethanol and subsequently freeze-dried. The crude extract and the enriched fraction were evaluated in terms of total phenolics and flavonoids according to reported methodologies [3], and the anti-tumoral activity was also evaluated.

A pancreatic cancer cell line (AsPC-1) was used for the antitumoral assay and performed as follows: after achieving high confluence (>90%), cells were exposed to the extracts (0.1 and 1 mg/mL, w/v) for 24h. Then to assess cell viability, cellular leakage of lactate dehydrogenase (LDH) was determined. Culture growth was defined by the sulforhodamine B assay (SRB), which reports on intracellular protein content. A ^{3}H-thymidine incorporation assay to determine cell proliferation rates was performed by liquid scintillation counting (LKB Wallac 1209 Rackbeta, Turku, Finland). The results were normalized for total protein content.

The hydroethanolic extract yield was almost 58%, and the enrichment yield almost 36%. A slight decrease was observed in total flavonoids (from 24.74 mg/L to 21.26 mg/L) and a significant increase was observed in the total phenolic compounds (from 34.93 to 77.84 mg/L) corresponding to hydroethanolic extract and phenolic-rich fraction, respectively.

The hydroethanolic extract and the phenolic-rich fraction showed a considerable effect on cell viability at both concentrations, with strong cytotoxic activity. However, the antiproliferative properties were concentration-dependent.

The antitumoral results show that both hydroethanolic extracts and phenolic-rich fraction could have remarkable activity in inhibiting cancer cell proliferation and tumor growth.

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Effect of pre-harvest foliar application of seaweed and glycine-betaine-based biostimulants on blueberry quality

T. Lopes[1,*], A. Silva[1,2], A. Aires[1,2], R. Carvalho[2], A. Vicente[3], B. Gonçalves[1,4]

[1]Centre for the Research and Technology of Agro-Environmental and Biological Sciences, CITAB, Institute for Innovation, Capacity Building, and Sustainability of Agri-food Production, Inov4Agro, University of Trás-os-Montes e Alto Douro, Quinta de Prados 5000-801, Vila Real, Portugal
[2]Departament of Agronomy, School of Agrarian and Veterinary Sciences, University of Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801, Vila Real, Portugal
[3]CEB, Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[4]Departament of Biology and Environment, School of Life and Environmental Sciences, University of Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801, Vila Real, Portugal
**tiagolopes97@hotmail.com*

Blueberry fruits have acquired a marked interest during the last decade, increasing the area and production of this fruit worldwide, including in Portugal [1]. In addition, blueberry is a product of interest due to its attractive taste and nutritional and health benefits [2, 3], being a rich source of phenolic compounds and vitamin C, well known for their high antioxidant activity [4]. These contents depend on various factors, e.g. edaphoclimatic conditions and agronomic practices. However, the fruit sector deal with global challenges, and new strategies looking to improve the recognized quality of blueberry should be found. Thus, it is imperative to use preharvest innovative crop strategies to improve the quality of fruits, increasing their value.

This work aimed to study the effect of preharvest foliar application of two biostimulants, an algae-based seaweed extract, and glycine-betaine, on the quality of two blueberry cultivars: 'Duke' and 'Draper'. Experiments were carried out in an orchard located at Vilarandelo, municipality of Valpaços, Portugal, comparing seven treatment modalities, one of which was a control treatment (T0). Three leaf applications were carried out, with two concentrations in the form of a commercial product based on the *Ecklonia maxima* macroalgae (EM), at doses of 4 L/ha (T1) and 2 L/ha (T2), a commercial glycine-betaine-based product (GB), at doses of 4 kg/ha (T3) and 2 kg/ha (T4), the junction of 4 L/ha EM + 4 kg/ha of GB (T5) and 2 L/ha of EM + 2 kg/ha GB (T6). Biometric and chemical (phenolic composition, vitamin C and antioxidant capacity) analyses were performed in this study.

In both cultivars, fruits treated with algae (T1 and T2) were heavier and fruits treated with the high dose of the two biostimulants (T5) had higher height, while the fruits with T1 presented higher width. The total phenolics content of the 'Duke' blueberries was higher with the application of the low dose of algae (T2) and with the high dose of the two biostimulants (T5). The application of algae (T1 and T2) and the junction of the two products (T5 and T6) increased the vitamin C content of 'Draper' fruits. The 'Duke' blueberries sprayed with a high dose of algae (T1) and with the junction of the two biostimulants (T5) had the highest antioxidant activity. In conclusion, although with differentiated influence and depending on the cultivars, this study showed that the application of these compounds can improve the quality attributes of two important blueberry cultivars.

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Determination of CO_2 in roasted coffee using a TAS optimized with super-modified simplex

Margarida Q. M. Silva[1], Inês M. Valente[1,2], P. J. Almeida[1], J. A. Rodrigues[1], João Rodrigo Santos[1,*]

[1]REQUIMTE/LAQV - Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, Porto, Portugal
[2]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar,
Universidade do Porto, Porto, Portugal
*jrodrigosantos@fc.up.pt

During the coffee roasting process, carbon dioxide is formed reaching ca. 1-2% w/w of the final product [1]. Carbon dioxide content in roasted coffee is important for three main reasons [1,2]: i) it plays a crucial role in coffee's crema formation and volume; ii) it can be correlated with the freshness of roasted coffee; iii) it delays the atmospheric oxygen contact with roasted coffee and consequent staling of this product.

The analytical methodologies to determine carbon dioxide in roasted coffee are scarce being the Hinman procedure – a gravimetric procedure – generally used. In the Hinman procedure, the coffee sample is immersed into an acidified solution to promote the evolution of carbon dioxide and, thereafter, by means of a nitrogen stream, the evolved carbon dioxide is dragged into a trap containing silica coated with sodium hydroxide. The mass change of the trap correlates with the amount of carbon dioxide present in the coffee sample. This procedure is, however, time consuming and laborious.

In this work, a total analysis system (TAS) was implemented to determine carbon dioxide content in roasted coffee. The TAS relied on a multicommutation flow system, featuring a reaction vessel with a gas diffusion flow cell and a spectrophotometric detector. In the reaction vessel, the acidification of the coffee sample takes place and the evolved carbon dioxide, collected by pervaporation in the acceptor solution (present in the gas diffusion flow cell), is determined by spectrophotometry. The operator only needs to weigh the coffee sample in this analysis.

The experimental parameters studied were the sample mass, pervaporation period and the acceptor solution composition. The latter parameter was studied using the super-modified simplex experimental design. The minimum quantity of detected CO_2 was 4.62×10^{-7} mol, the solutions consumption was 24.7 mL *per* analysis and the analysis rate was 7 samples *per* hour. Several coffee samples presenting different roasting intensities were analysed by the developed system and the Hinman methodology. The results obtained by both approaches showed that a linear correlation could be established.

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Phenolic compounds and antioxidant and cytotoxic properties of maritime pine (*Pinus pinaster* Ait.) bark extracts

José I. Alonso-Esteban[1,2,3,*], Tiane C. Finimundy[1,2], Carla Pereira[1,2], Manuela Vaz Velho[4], Josiana Vaz[1,2], Márcio Carocho[1,2], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Departamento de Nutrición y Ciencia de los Alimentos, Facultad de Farmacia, Universidad Complutense de Madrid, Plaza Ramón y Cajal, s/n, 28040 Madrid, España
[4]Centro de Investigação em Sistemas Agroalimentares e Sustentabilidade (CISAS), Instituto Politécnico de Viana do Castelo, Rua Escola Industrial e Comercial Nun'Álvares, 34, 4900-347 Viana do Castelo, Portugal
*joseigal@ucm.es

Maritime pine (*Pinus pinaster* Ait.) is a pine species native to the western Mediterranean basin which has an economic importance in southwestern Europe due to the industrial uses of its wood. Other parts of the tree, including the bark, are considered by-products, and they stand out because of the presence of secondary metabolites, such as phenolic compounds. These compounds have biological potential, making them suitable to produce food supplements and functional foods, among other applications [1].

Two extracts were obtained from maritime pine bark by microwave assisted extraction (MAE) and ultrasound assisted extraction (UAE), and their phenolic compound content and antioxidant and cytotoxic properties were analysed. Phenolic compounds analysis was carried out by HPLD-DAD-ESI/MS [2]. Antioxidant properties were measured via thiobarbituric acid reactive substances (TBARS) formation inhibition method in brain cell homogenates, cellular antioxidant activity (CAA) in murine macrophage cells RAW 246.7, and oxidative haemolysis inhibition assay (OxHLIA) in sheep blood erythrocytes [2,3]. The cytotoxic properties of the extracts were screened in tumour and non-tumour cells by the sulforhodamine B assay [3].

The MAE showed a greater yield of extraction, three times higher than UAE. Major phenolic compounds in maritime pine extracts were catechin and B-type procyanidins, and some A-type procyanidins and taxifolin derivatives were also found in both extracts. The best antioxidant activity results were observed in the TBARS method and OxHLIA, especially in the case of the extract obtained by MAE, although it did not showed CAA at the maximum concentration studied (2 mg/mL), unlike the extract obtained by UAE, which showed some activity at that concentration. Regarding cytotoxic properties, the two extracts showed similar results since they presented activity in tumour and non-tumour lines with IG_{50} values higher than those observed with the positive control (ellipticine). Therefore, MAE was a better extraction method for obtaining a functional extract from maritime pine bark.

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Effects of different treatments on the phenolic composition of acorn extracts from *Quercus robur* and *Quercus rotundifolia*

José I. Alonso-Esteban[1,2,3,*], Cristiano G. S. Mateus[1,2], Tiane C. Finimundy[1,2], Daniele B. Rodrigues[1,2], Pedro Babo[4], Raphaël Canadas[4,5], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Alameda Santa Apolónia, 5300-253 Bragança, Portugal;
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[3]Departamento de Nutrición y Ciencia de los Alimentos, Facultad de Farmacia, Universidad Complutense de Madrid, Plaza Ramón y Cajal, s/n, 28040 Madrid, España
[4]Landratech, Lda., Largo do Esteiro 6, 2050-261 Azambuja, Portugal
[5]Tech4MED™, UPTEC, ASPRELA I, Office-Lab 0.16, Business Campus, n.° 455/461, 4200-135 Porto, Portugal
*joseigal@ucm.es

The European oak (*Quercus robur* L.) and the holm oak (*Quercus rotundifolia* Lam.) are two examples of endemic species that already contribute for the socio-economic development of the Iberian Peninsula. The first one stands out because of its wood, and the second one has been traditionally managed as savannah-like ecosystems for livestock breeding [1]. However, from a chemical perspective, the potential of these plants, especially their acorns, can be further expanded.

For this work, acorn samples of the two mentioned species were submitted to four different extraction methods in order to characterize the phenolic compounds of each extract. The four extractions were the following: 1 – maceration with water at 40 ºC for one hour; 2 – infusion with boiling water for 5 minutes; 3 – decoction with boiling water for 5 minutes; 4 – maceration with ethanol 80% (v/v) at room temperature for 1 hour. The extractions were performed using a solid/liquid ratio of 25 g/L and the phenolic compounds were analyzed by HPLD-DAD-ESI/MS [2].

The average extraction yields ranged between 9.58 – 21.89 g of extract/100 g for *Q. robur* and from 2.88 to 6.82 g of extract/100 g for *Q. rotundifolia*. Regarding the composition of phenolic compounds, gallic and ellagic acids were the most abundant molecules found in the samples of these species [3]. The total content of phenolic compounds varied between 71 - 124 mg/g of extract and 70 – 90.5 mg/g of extract in *Q. rotundifolia* and *Q. robur*, respectively. Gallic acid was the compound which was found in the greatest concentration in all the extractions, reaching its maximum concentration when the aqueous maceration extraction was applied. Ellagic acid and its derivatives (ellagitannins) were also found in the extracts, but to a lesser extent than gallic acid.

Considering the extraction yield and the content of phenolic compounds, the most promising extraction method was the aqueous maceration, which could be applied to obtain extracts rich in gallic acid and ellagitannins from acorns.

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Synergy and antagonism: a different interpretation of the interactions between the antioxidants used as food additives

M. Carpena[1], L. Cassani[1,2,3], P. Garcia-Oliveira[1,2], M. Fraga-Corral[1,2], Paz Otero[1], R. Perez-Gregorio[1,8], Hui Cao[1,5], Jianbo Xiao[1,6], J. Simal-Gandara[1,*] and M.A. Prieto[1,2,*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.
[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal.
[3] Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA, CONICET), Colón 10850, Mar del Plata (7600), Argentina
[4] LAQV-REQUIMTE Department of Chemistry and Biochemistry. Faculty of Sciences. University of Porto. Rua do Campo Alegre s/n 4169-007 Porto, Portugal.
[5] College of Food Science and Technology, Guangdong Ocean University, Zhanjiang, Guangdong, China.
[6] International Joint Research Laboratory of Intelligent Agriculture and Agri-products Processing, Jiangsu University, Zhenjiang, China.
**Corresponding authors: mprieto@uvigo.es and jsimal@uvigo.es*

The food industry uses diverse additives with antioxidant properties to extend the shelf-life of food products. However, even though these compounds are added attending to their individual benefits, their combinatory effects are not considered in most cases. Performing all the assays to analyze the different possible interactions would be time-consuming, nevertheless, a study based on binary combinations could help to predict the expected results and implications of using these molecules. In this context, even though the concepts of synergy and antagonism have been frequently used to describe these relations, they are usually badly applied on simple relations and inadequately designed experiments and forget considerations of toxicological risk assessment. In this study, the antioxidant activity of seven compounds commonly used as antioxidant agents in the food industry has been assessed to analyze the resulting interactions when combined with trimethyl-quinoline (TMQ) or butyl-hydroxytoluene (BHT) or a combination of both (TMQ+BHT). The responses were measured by different antioxidant assays (DPPH, ABTS, Crocin, and β-carotene). For the development of the experiment, a *response surface methodology* (RSM) was applied to estimate the coefficients of the selected parameters, *i.e., K* (nM radical reduced); *τ* (µg of A); *vt* (averaged molecules of the reduced radical/µg of A), both if assuming interactions and if not, to evaluate the positive or negative effects of their combined applications in terms of their resulting antioxidant activity. The results of the experiments showed statistically consistent responses of null, synergy and antagonism effects when characterizing the interactions between several pairs of individual and complex mixtures of chemical antioxidant agents.

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Sargassum muticum - Screening of its bioactive potential

<u>Aurora Silva</u>[1,2]; L. Cassani[1,3,*]; M. Carpena[1]; Hui Cao[1]; Paz Otero[1]; C. Lourenço -Lopes[1]; P. Garcia-Perez [1,4], Clara Grosso[2]; S. Baamonde [5], F. Fernandez-Saa [5], M. Fátima Barroso[2]; J. Simal-Gandarra[1]and M.A.Prieto[1,2,*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.
[2] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr António Bernardino de Almeida 431, 4200-072 Porto, Portugal.
[3] Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA, CONICET), Colón 10850, Mar del Plata (7600), Argentina.
[4] Department for Sustainable Food Process, Università Cattolica del Sacro Cuore, Via Emilia Parmense 84, 29122 Piacenza, Italy.
[5] Centro de Investigación e Innovación Tecnológico en Algas Marinas (CIITAM), Algas Atlanticas Algamar S.L., Polígono de Amoedo, E-36840 - Pazos de Borbén (Pontevedra), Spain.
Corresponding authors: <u>luciavictoria.cassani@uvigo.es</u> and <u>mprieto@uvigo.es</u>

Sargassum muticum (Yendo) Fensholt is an invasive brown macroalga native from Japan. However, it is one of the most present Sargassum species on the European coasts causing a serious environmental problem since it can disturb the marine ecosystem, disrupting the normal development of native species. In this framework, there is a huge interest in the research of possible applications to this biomaterial. *S. muticum* is an unexplored natural source of bioactive compounds and with high value to pharmaceutical and biotechnology industries.

For that purpose, four different experimental approaches were carried out: i) evaluation of the scavenging capacity of reactive oxygen species; ii) assessment of the inhibition capacity towards enzymes involved in human health; iii) antimicrobial activity; iv) anti-proliferation of the lung (A549), liver (HEPG2), and gastric cancer (AGS) cells lines. Our results showed an important scavenging activity to nitric oxide (IC_{50} 0.17 mg/mL), superoxide (IC_{50} 0.016 mg/mL), Hydroxyl (IC 50 1.08 mg/mL) radicals and 0.2mg/ml towards the hydrogen peroxide specie. *S. muticum* also reveals some activity in the inhibition of acetylcholinesterase, butyrylcholinesterase, and monoamine oxidase but being especially active in the tyrosinase (IC_{50} of 0.332 mg/mL) expression. All these enzymes are related to brain disorders and IC_{50} of 0.053 mg/mL was determined to α-amylase an enzyme involved in the diabetes mellitus. Concerning the antimicrobial activity, the *S. muticum* extract affected two of the six strains tested causing the inhibition growth of *Staphylococcus aureus* and *Salmonella enteritidis*. Moreover, the experiment realized on eternal cell lines have undisclosed a potential as a cytotoxic agent since they present IC_{50} of 154 ug/mL to A549; 50.27 ug/mL to HEPG2, and 44.43 to AGS cell line.

The results allow to foresee an application of *S. muticum* extract as natural antioxidant additive, and as nutraceutical since is active in depletion of the health -related enzymes and is cytotoxic towards some cancer cells.

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Fermentation of olive pomace paste to obtain an innovative antioxidant food ingredient

Josman Dantas Palmeira[1,2], **Rita C. Alves**[3], **Maria Beatriz P. P. Oliveira**[3] **and Helena M. N. Ferreira**[1,2]

[1]UCIBIO - Applied Molecular Biosciences Unit, REQUIMTE – University of Porto, Porto, Portugal
[2]Microbiology, Biological Sciences Department, Faculty of Pharmacy – University of Porto, Porto, Portugal
[3]REQUIMTE/LAQV, Faculty of Pharmacy, University of Porto, Porto, Portugal
**josmandantasp@gmail.com*

Background: Olive oil is an important Mediterranean traditional food which consumption and processing are increasing in Portugal and worldwide. Along with its production, several by-products are generated such as olive mill wastewaters and olive pomace (OP). OP is a by-product that includes high levels of polyphenols with recognized antioxidant activity, and a low-cost source of natural compounds with high interest for food industry. After stone pieces remotion originates olive pomace paste (OPP) is obtained [1]. Our study evaluated the potential of the spontaneous fermentation (SF) of OPP as a process of valorisation of OP as a new food ingredient.

Methods: OPP was collected in January of 2022 in the North of Portugal (Alfândega da Fé). SF was promoted in different temperature conditions, namely, 4°C, room temperature (RT, 25 to 30°C) and 37°C, for 32 days (d). The total count of microorganisms was evaluated at 6 moments of fermentation (0h, 48h, 96h, 8d, 16d and 32d), by surface spread in plate count agar. The counting methodology was done in triplicate and the incubation at 37°C overnight.

Results: The results showed that, in general, the SF of OPP promotes the growth of the natural flora of this by-product. A total of 48h was enough to change the natural flora, highlighting the 37°C with $4,3\text{x}10^5$ total microorganisms growth in the fermented OPP.
The microbiological flora changes with the used temperature conditions. The 37°C fermented product presented a fast profile of fermentation, with a decreasing tendence of total microorganisms after 48h. The RT fermented product showed a slow profile of fermentation, with a continuous increasing of microbial population until the 16th day. The evaluation of polyphenols level after fermentation is ongoing to determine the impact of fermentation in the antioxidant features of OPP.

Conclusions: This exploratory approach of SF of OPP shows that this by-product has the potential to be transformed into a new food product, with promising results, with fast or slow fermentation depending on temperature conditions. This represents a new approach for agro-industrial Mediterranean by-products valorisation, relevant in terms of food security and environmental sustainability.

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Study of the antioxidant, antimicrobial and anti-inflammatory activities of two *Euphorbia* species

Ana Perez Vazquez[1], Paula Barciela Alvarez[1], Tayse Ferreira F. da Silva[2,3], Daniele B. Rodrigues[2,3], Filipa Mandim[2,3], Tânia C. Pires[1,2,3], Maria Carpena [1], Jesus Simal-Gandara[1], Lillian Barros[2,3*] and Miguel A. Prieto [1,2,*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.
[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Aplónia, 5300-253 Bragança, Portugal.
[3] Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apólonia, 5300-253 Bragança, Portugal.
* lillian@ipb.pt, *mprieto@uvigo.es

In this research, a study of the antioxidant, antimicrobial and anti-inflammatory activities of two *Euphorbia* species (*Euphorbia hirta* and *Euphorbia jolkinii*) was developed. *Euphorbia* species belong to the *Euphorbiaceae* family, being commonly found in America and tropical Africa. *Euphorbia* species have been traditionally used in folk medicine to treat gonorrhea, migraines, intestinal parasites, warts, and skin diseases [1]. Since there is more data available of *Euphorbia hirta,* the aim of this study was to provide a comparison between *E. hirta* and *E. jokinii* regarding their antioxidant, antimicrobial and anti-inflammatory activities. For the cellular antioxidant activity, murine macrophage cells RAW 264.7 were used following the procedure described by Wolf & Lui (2007). *E. hirta* showed better inhibition percentage results than *E. jolkinii*, being 2,000 µg/mL, the maximum concentration tested for both samples. Extracts of both *Euphorbia* species were used to determine their antimicrobial activity. Gram-negative and Gram-positive food and clinical bacteria were tested for this assay. Moreover, Streptomycin, Methicillin and Ampicillin were used as controllers to compare both MIC and MBC results. For the food bacteria, *E. jolkinii* had better MIC results than *E. hirta* when Gram-negative bacteria were tested, although it was lower than controllers. MBC results for both *Euphorbia* species were similar and lower than the controllers. When Gram-positive clinical bacteria were tested, similar MIC results between both extracts were obtained. However, when *L. monocytogenes* and *S. aureus* were tested, *E. jolkinii* showed better MIC results. Antifungal activity was also assessed using ketoconazole as control and *Aspergillus brasiliensis* and *Aspergillus fumigatus* as fungi. Unsatisfactory results were obtained for both *Euphorbia* species for both fungi. AGS, CaCo2, MCF-7, NCl-H460, PLP2 and RAW 264.7 cell lines were used for the anti-inflammatory assay. Ellipticine was used as control in all the cell lines except in RAW 264.7, where dexamethasone was used. Results showed lower anti-inflammatory activity of the 2 extracts compared to the controllers in all cell lines, being *E. jolkinii* the one with lower GI_{50}. Considering the obtained results, although *E. hirta* has been widely studied, *E. jolkinii* showed better antimicrobial and anti-inflammatory activities, being a suitable option for the pharmacological industry.

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ALM65

Verbascum sinuatum L.: Potential source of natural antioxidant compounds for food and pharmaceutical industries

P. Donn[1], F. Chamorro [1], S.S. Mansour[1], A. Perez-Vazquez[1], P. Garcia-Oliveira[1,2], J. Echave[1], P. Garcia-Perez [1,3], J. Simal-Gandara[1,*], M.A. Prieto [1,2] and L. Cassani[1,2,*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.

[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal.

[3] Department for Sustainable Food Process, Università Cattolica del Sacro Cuore, Via Emilia Parmense 84, 29122 Piacenza, Italy.

**Corresponding authors: jsimal@uvigo.es* and luciavictoria.cassani@uvigo.es

The pharmaceuticals and food industries are increasingly interested in ingredients from natural sources to cope with the adverse effects of synthetic chemical ingredients. Thus, this work explored the potential of *Verbascum sinuatum* L. flowers (VSF) as a natural ingredient in the designing of food preservatives, and formulation of functional foods and pharmaceutical products.

To this aim, heat-assisted extraction (HAE) was applied to *Verbascum sinuatum* L. flowers to obtain an antioxidant-rich extract. Dried flowers of *V. sinuatum* L. were mixed with aqueous methanol (60%), at a solid/solvent ratio of 50 g/L. Then, HAE was applied at 50° C for 1 h under continuous agitation (1500 rpm). The obtained extract was centrifugated, filtrated, and stored at 80°C until analysis. The extraction yield, total phenolic content (TPC), total flavonoid content (TFC), and *in vitro* antioxidant activity (measured through the scavenging activity against DPPH, and ABTS radicals, and crocin bleaching assay) of the VSF extract were determined.

The extract concentration of VSF was 10.58 ± 1.65 mg/mL and the extraction yield was 24.78 ± 3.64% w/w. Additionally, TPC and TFC were 19.19 ± 1.72 mg GAE /g dw and 124.37 ± 21.53 µg QE /g dw, respectively, suggesting that VSF extract is an interesting source of polyphenolic compounds. Regarding antioxidant activity, VSF showed antioxidant activity with better DPPH radical quenching ability than ABTS radicals since the extract concentration required to scavenge 50% of both radicals (IC_{50}) was 0.230±0.090 mg/mL for DPPH and 0.375±0.069 for ABTS. Concerning the crocin bleaching inhibition assay, VSF was able to delay crocin oxidation by 50% up to 653.80 ± 126.96 min/mg of extract.

Overall, this work revealed that VSF are a valuable source of natural antioxidant compounds with potential applications as functional food ingredients or additives in the food industry, and for the development of drugs in pharmaceutical industry.

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Exploring the potential of *Citrus aurantium* L. flowers as a source of antioxidant compounds

S.S. Mansour[1], F. Chamorro[1], P. Donn[1], P. Barciela-Alvarez[1], M. Carpena[1], A.G. Pereira[1,2], Paz Otero[1, 2], J. Simal-Gandara[1], M.A. Prieto[1,2 *] and L. Cassani[1,2*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.
[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal.
**Corresponding authors: mprieto@uvigo.es and luciavictoria.cassani@uvigo.es*

Plant-based natural bioactive compounds have a lot of interest due to their multifunctional properties and potential as nutraceuticals. The flowers of *Citrus aurantium* L. (Bitter orange) are considered as a promising natural source of ingredients in the development and formulation of functional foods and pharmaceutical products.

This study aimed to investigate the potential *in vitro* antioxidant activity of *C. aurantium* L. flowers. For this purpose, dried flowers of *Citrus aurantium* L. were mixed with aqueous methanol (60%), at a solid/solvent ratio of 50 g/L. Next, heat assisted extraction (HAE) was applied at 50°C for 1 h under continuous agitation (1500 rpm). Once the extract was obtained, it was centrifuged, filtered, and stored at 80°C until analysis.

Total phenolic content (TPC), and total flavonoid content (TFC) were measured by the Folin-Ciocalteu colorimetric assay and aluminum chloride colorimetric method, respectively. The extraction yield was gravimetrically determined. The antioxidant activity was evaluated through the scavenging activity against 1,1-diphenyl-2-picrylhydrazyl (DPPH) and ABTS radicals and results were expressed as the effective extract concentration required to scavenge 50% of DPPH and ABTS radicals (IC_{50}).

Results indicated that high extraction yield was obtained (54.64 ± 4.59% w/w). Concerning polyphenols content, TPC and TFC were 18.22 ± 1.44 mg GAE /g dw and 111.44 ± 20.60 µg QE /g dw, respectively, thus confirming the efficiency of the extraction procedure in extracting bioactive compounds. A comparison between DPPH and ABTS radical quenching results suggests that flower extracts had a better ability to quench ABTS radicals than DPPH radicals since IC_{50} values were 0.402±0.081 mg/mL and 0.977±0.089 mg/mL, respectively.

In conclusion, results suggest that *Citrus aurantium* L. flowers are a rich source of extractable polyphenolic compounds that can be further purified to be used in food and medicine industries as natural preservatives.

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ALM67

Biological properties of *Hypericum sampsonii* and *Hypericum japonica*: comparison of the antioxidant, anti-inflammatory and antimicrobial activity

Paula Barciela Alvarez[1], **Ana Perez Vazquez**[2], **Daniele B. Rodrigues**[2], **Tayse Ferreira F. da Silva**[2], **Filipa Mandim**[2], **Tânia C. Pires**[2], **Maria Carpena** [1], **Jesus Simal-Gandara**[1], **Lillian Barros**[2,*] **and Miguel A. Prieto** [1,2,*]

[1] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E32004 Ourense, Spain.
[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal.
* *lillian@ipb.pt*, **mprieto@uvigo.es*

Hypericum was famous in ancient times for its properties, morphology, and adaptability. Currently, it has naturalized in practically all parts of the world from America to Australia. It is considered a cosmopolitan species present on all five continents. *Hypericum* is the largest genus of the *Hypericaceae* family (more than 500 species classified in 36 taxonomic sections). The study of these ethnomedicinal plants has been developed mainly and traditionally in China where there are more than 64 species, of which 19 have been related to the presence of phytochemicals with anti-tumor, anti-inflammatory, antimicrobial, antidepressant, analgesic, or neuroprotective properties, among others [1]. Remarkably, the great potential of these species has hardly been scientifically evaluated [2].

In this study, the comparison and study of the different biological properties of the species *Hypericum japonica* and *Hypericum sampsonii* was carried out. Cellular antioxidant activity was evaluated with murine macrophage cells, with both species showing 77±5% inhibition at a maximum tested concentration of 2,000 µg/mL. Antimicrobial activity was evaluated on both food contaminants and clinical bacteria and fungi. MIC and MBC were determined by colorimetric assay, where 10 µL of liquid was added from each well that showed no color change was plated on solid medium, blood agar (7% sheep blood) and incubated at 37°C for 24 h, respectively. Ampicillin and Steptomicin were used for all bacteria tested and Methicillin was also used for *Staphylococcus aureus*. The MIC results showed that *H. japonica* has a higher antimicrobial effect on Gram-negative bacteria and in *Enterococcus faecalis*. While H. *sampsonii* showed a more effective power for the rest of Gram-positive tested bacteria. The antifungal activity was performed applying the method described by Heleno et. al., 2013, using *Aspergillus brasiliensis* and *A. fumigatus* and using Ketoconazole as positive control, showing no activity for both species [3]. Anti-inflammatory activity was studied using six cell lines (CaCo2, MCF-7, NCl-460, PLP2, RAW 264.7) and Ellipticine as a control in all but RAW 264.7 where Dexamethasone was used. For all cell lines, both *Hypericum* species showed lower GI_{50} than the control, being *H. japonica* the one with higher anti-inflammatory effect of the two extract samples. This study is the first to provide more information on the bioactivities of two less-analyzed *Hypericum* species.

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Insights of honey DNA extraction methods for plant species identification of honey from Natural Park of Montesinho

Leandro Magalhães[1], Sónia Soares,[1,*], Cristina Delerue-Matos[1]

[1]REQUIMTE/LAQV – Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal
**sonia.soares@graq.isep.ipp.pt*

Honey is a sweet natural food product, produced by honey bees from the nectar of plants and/or secretions of living parts of plants. Before honey bees store it inside the beehive, the collected nectar is broken into simple sugars by enzymes that can be found in bee's saliva. This product is composed essentially by simple sugars (68%) and water (18%) and smaller quantities of other minor compounds such as vitamins, minerals, proteins, organic acids, phenolic compounds, among others [1]. The presence of these compounds in honey are highly dependent of the plant species visited by honey bees and its distribution confer to honey different and distinct organoleptic and antioxidant, antibacterial, and anti-inflammatory properties [1]. This strict relation of botanical origin and its biological and organoleptic properties lead to a quality distinction of honey types. Usually, monofloral honeys (generally honey with at least 45% of pollen grains of one single plant species [2]) are perceived as high-quality products due its particular flavor and taste and specific biological properties, being thus are highly sought after and attaining high market values. The same happen with honeys produced in specific regions attains the denomination of Protected Designation of Origin (PDO), as honey produced in Natural Park of Montesinho (NPM).

Thus, the assessment of the botanical origin of honey is extremely important regarding consumers and producers' interests. Traditionally, this analysis is performed trough melissopalynology studies [3]. This technique consists in the analysis of pollen content and fungal spores in honey. However, these methods require appropriate skills and high-end equipment and is time-consuming. As alternative, DNA-based methods are promising, as these methods are simple, fast and precise. Moreover, DNA molecule proved to be stable at adverse conditions, including food processing. Briefly, DNA based methods consist in DNA isolation and extraction, PCR amplification of particular genetic markers containing DNA fragments, and identifying DNA profiles defined by those markers. In honey matrix, some difficulties could compromise the success of DNA extraction and analysis, such as the pollen grain structure and components, and the presence of several cell components, including polysaccharides, proteins, and DNA polymerase inhibitors, such as alkaloids and polyphenols [3]. Thus, a previously sample treatment for the extraction of genetic material is imperative in the case of honey and its related products.

In this work, we compare different conditions in honey pre-treatment for posterior DNA extraction with the commercial kit NucleoSpin Plant II (Machery-Nagel). Different quantities of honey, different times of ultrasounds and the use of PBS for dissolve and wash honey, were used in each honey sample from NPM. The quality of DNA extracts was assessed by spectrophotometry and electrophoresis. Results revealed that honey pre-treatment using ultrasound produces acceptable yields and purity. Additionally, a PCR amplification using universal primers targeting the gene 18S rRNA was performed to evaluate amplifiability of the extracted DNA. As expected, all extract samples revealed to have amplifiable DNA. Combining a simple and easy to perform honey pre-treatment with an effective DNA extraction method, allows us to get desired good extracts for honey. Thus, this methodology is the first step for further studies involving species identification in honey regarding honey quality assessment.

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Efeito do método de extração no perfil fenólico e na atividade antioxidante de extratos de casca de marmelo

Alexis Pereira[1,2], Souha Othman[1], Mikel Añibarro-Ortega[1,2], Maria Inês Dias[1,2], José Pinela[1,2,*], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
**jpinela@ipb.pt*

O marmelo é o fruto de uma pequena árvore decídua (*Cydonia oblonga* Mill.) nativa do Cáucaso e cultivada em vários países, incluindo Portugal. Devido ao seu sabor amargo e adstringente, o marmelo é geralmente processado em produtos alimentares açucarados, tais como a marmelada, um doce típico português. Durante a confeção deste alimento, a casca deste fruto é frequentemente descartada como subproduto. Apesar disso, estudos anteriores apontaram que a casca do marmelo possui compostos bioativos com efeitos promotores de saúde, bem como propriedades bioativas [1]. Assim, este trabalho teve como objetivo comparar o perfil fenólico e a atividade antioxidante *in vitro* de extratos de casca de marmelo obtidos por maceração dinâmica hidroetanólica (1 h + 1 h de extração) e decocção (5 min de fervura + 5 min de repouso). Para isso, o rendimento de extração foi avaliado gravimetricamente e os compostos fenólicos detetados nos extratos foram caracterizados por HPLC-DAD-ESI/MS^n [2]; a atividade antioxidante *in vitro* foi avaliada através do ensaio de inibição da formação de substâncias reativas aos ácido tiobarbitúrico (TBARS) e da hemólise oxidativa [2]. A análise cromatográfica permitiu identificar três classes de compostos fenólicos, nomeadamente ácidos fenólicos, flavonóis e flavan-3-óis. O conteúdo de compostos fenólicos foi de 4,70 mg/g no extrato hidroetanólico e de 4,27 mg/g no extrato aquoso. O extrato hidroetanólico foi mais eficaz em inibir a peroxidação lipídica e a hemólise oxidativa do que o extrato preparado por decocção, o que concordou com os maiores teores de flavan-3-óis. Embora os métodos de extração testados tenham empregue diferentes solventes, tempos de processamento e temperaturas, a maceração dinâmica hidroetanólica foi mais adequada para obter extratos com maiores teores de polifenóis e maior atividade antioxidante. Assim, os resultados evidenciaram que o método de extração afeta a extração de compostos fenólicos e, consequentemente, a atividade antioxidante. Desta forma, a casca do marmelo poderá ser reinserida na cadeia de valor através da sua reutilização em ingredientes naturais antioxidantes para alimentos e bebidas.

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ALM70

Priming with *Laminaria* extract to boost tomato performance and mitigate drought effects

M. Pereira[1], A. R. Circuncisão[1], M. C. Dias[2], P. Pinto[3], C. Santos[3], A. M. S. Silva[1], S. M. Cardoso[1], S. Silva[1,*]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]Department of Life Sciences, Centre for Functional Ecology, Faculty of Sciences and Technologies, University of Coimbra, Calçada Martim de Freitas, 3000-456 Coimbra, Portugal.
[3]Department of Biology, Faculty of Sciences, LAQV-REQUIMTE, University of Porto, Rua do Campo Alegre 4169-007, Porto, Portugal.
**soniasilva@ua.pt*

The UN 2030 Agenda fosters the food security and sustainable agriculture, and simultaneously, the world is facing now the acceleration of climate change episodes which will conduct to the loss of a percentage of arable worldwide. These challenges urge developing new sustainable strategies enabling crops to combine high productivity and tolerance to abiotic stressors, namely drought. In this context, this work targeted the benefits of the brown seaweed *Laminaria digitata* aqueous extract, obtained in cold water, 1:7 (w/v), against drought effects and to improve plant performance. Thus, *Solanum lycopersicum* (tomato) plants were primed with solutions of 0, 0.1, and 1 g/L of *L. digitata* aqueous extract (900 µL per plant) for 5 days and, afterwards, were divided in two groups: water stressed (WS) and well-watered (WW). The WS group wasn't watered for a week while the WW group continued being irrigated. At the end of the stress period, the leaves were analyzed for their morphological and physiological traits, and phytohormones content.

The extract used contained 27.7 % ash, 4.8% protein, and 38.5 % of total sugars. Besides, the amounts of total phenolic compounds and of phorotannins accounted for 1.3 g phloroglucinol equivalents/100g extract of total phenolics and 0.26 g phloroglucinol equivalents /100g extract, respectively. The foliar application of the *L. digitata* extract did not alter the tomato plant growth, leaf water content, neither proline or H_2O_2 contents. Nevertheless, *L. digitata* treatment stimulated gas exchange in the WW group, with the increment of the net CO_2 assimilation rate (P_N), stomatal conductance (g_s), intracellular CO_2 concentration (C_i), and transpiration rate (E) in both concentrations. Overall, there was a decrease of g_s and E in both concentrations and P_N in the highest dose, in the WS group. Despite that, the water use efficiency showed a trend to increase in this group, contrarily to the WW one. Concerning the fluorescence of chlorophyll *a*, a trend to increase the maximum efficiency of PSII (F_v/F_m) was detected in the WW group, despite a decrease of the effective efficiency of PSII (Φ_{PSII}), accompanied by the increase of the photochemical quenching (qP) and the decrease of the non-photochemical quenching (NPQ) at the lowest dose. At the same dose and in the WS group, the treatment enhanced the Φ_{PSII}, together with the increase of qP. Besides photosynthesis, *L. digitata* treatment also showed capability to modulate phytohormone contents, decreasing the content of jasmonic acid and of methyl ester jasmonic acid in all groups, and gibberellic acid (GA3) in WS. Besides, the WW leaves treated with 0.1 mg L^{-1} exhibited an increment of GA3 and 6-Benzylaminopurine, whereas 1 mg L^{-1} treatment decreased the salicylic acid content. Together, these results highlight the capability of *L. digitata* extract in modulating photosynthesis and phytohormones in tomato, thus pinpointing their potential use as plant biostimulant and to mitigate drought stress effects.

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Algae blend on lambs diet: Effects on rumen and colon fermentation pattern

Cátia S.C. Mota[1]*, Vasco A.P. Cadavez[2], Ursula Gonzales-Barron[2], Ana R.J. Cabrita[1], Helena Abreu[3], Joana L. Silva[4], António J.M. Fonseca[1], Margarida R.G. Maia[1]

[1]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal;
[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal;
[4]ALGAplus-Produção e Comercialização de Algas e seus derivados Lda, PCI, Via do Conhecimento, 3830-352 Ílhavo, Portugal;
[5]ALLMICROALGAE - Natural Products, SA, Rua 25 de Abril, 2445-413 Pataias, Portugal;
**catiam04@gmail.com*

The rumen harbors a complex microbial community that ferments dietary nutrients to volatile fatty acids (VFA) and synthesizes microbial protein, the main energy and protein sources to the ruminant host [1], along with enteric methane production. Moreover, microbial fermentation products of the lower gut are associated with intestinal and animal health [2]. Rumen and lower gut microbiota and fermentation parameters are known to be strongly influenced by diet, however the dietary inclusion of micro- and macroalgae blend has not yet been assessed. Thus, this study aimed to evaluate the supplementation effect with a commercial blend of micro- and macroalgae species (Algaessence™; Allmicroalgae and AlgaPlus, Portugal) on the rumen and colon fermentation profile of concentrate fed lambs.

Three groups of 10 Bordaleira-de-Entre-Douro-e-Minho lambs, males and females, were randomly assigned to one of three diets: i) pasture; ii) comercial concentrate diet, and iii) comercial concentrate diet with 5% algae blend. During the 60 days of the trial, lambs had *ad libitum* access to water and meadow hay. Lambs were slaughtered in a commercial abattoir and rumen and colon digesta samples were collected. Digesta pH was measured and ammonia-N and VFA were determined by spectrophotometry and gas chromatography, respectively [3]. Enteric methane production was calculated based on VFA stoichiometry [4]. Data were analyzed using the GLM Procedure (SAS Institute), and the model included the fixed effects of diet, gender and diet x gender interaction, and the random residual error.

Most rumen and colon fermentation parameters were affected by diet ($P < 0.05$), while gender had no effect ($P > 0.05$). An interaction between diet and gender was observed ($P \leq 0.007$) for isovaleric and valeric acids proportion. Compared to concentrate fed lambs, algae supplementation affected the proportion of most individual VFA. In the rumen, acetic acid increased ($P < 0.001$) and isobutyric and isovaleric acids proportion decreased ($P \leq 0.004$); butyric acid and acetic to propionic acid ratio being similar to those of concentrate and pasture fed lambs. The proportion of isobutyric, butyric, isovaleric and valeric acids in the colon were promoted by the supplementation with the algae blend ($P \leq 0.023$) when compared to concentrate fed lambs; acetic and propionic acids not differing from concentrate and pasture fed lambs. Algae supplementation had no effect ($P > 0.05$) on rumen methanogenesis.

The results of this study suggest a modulation effect of algae blend supplementation on the rumen fermentation pattern with potential impacts on lambs' health, thus pinpointing the importance to assess the effects of dietary inclusion of micro- and macroalgae on gut microbiota.

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Antioxidant activity of sweet cherry fruits (cv. *Lapins*) after foliar application of a seaweed extract

Sara Campos[1,*], Sílvia Afonso[2], Berta Gonçalves[2]

[1] University of Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal
[2]Centre for the Research and Technology for Agro-Environmental and Biological Sciences, CITAB, Institute for Innovation, Capacity Building and Sustainability of Agri-food Production, Inov4Agro, University of Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal
al66489@utad.eu

Sweet cherry has been used as a food source for humanity and other animals for thousands of years [1]. Currently sweet cherry trees are mostly cultivated in temperate regions and the three main worldwide producers are Turkey, EUA, and Chile [2] [3]. Sweet cherry fruits are one of the most popular fruits for consumers due to its organoleptic characteristics but also for their health benefits, which are associated with bioactive compounds and antioxidant activity [4] [5].

Synthetic fertilizers, plant growth regulators and other crop enhancers have been widely used during the past decades, but farmers started to look for environment friendly alternatives such as biofertilizers and biostimulants, which are known as a substance or microorganism that improves the nutrient uptake, the response to biotic and abiotic stress tolerance and the quality traits of the plant [6]. Seaweed extracts are included in this group as they contain amino acids, carbohydrates, proteins, osmo-protectors and hormones that contribute to controlling fruit set, improve fruit size and growth and enhance fruit quality [7].

In the present work, the main objective was to determine the influence of the pre-harvest application of a biostimulant on the chemical composition and antioxidant activity of sweet cherry fruits (cv. *Lapins*) collected at harvest, in a commercial orchard located in Resende – Portugal. Foliar application of two different concentrations of a seaweed-based biostimulant (*Ecklonia maxima*) (0.30% (Sw>) and 0.15% (Sw<)) on 8 trees per treatment were performed, at three different phenological stages: fruit about 70% of final size, beginning of fruit coloring and three days before fruit ripe for picking. Control was performed with water. The total phenolic, *O*-diphenol and flavonoid contents and antioxidant activity (FRAP and DPPH) were accessed. Regarding the total phenolic and flavonoid contents, the best results were observed with both concentrations of the seaweed-based biostimulants when compared to control. *O*-diphenols content presented better results for Sw<. For FRAP and DPPH methods higher antioxidant activity was also found for Sw< and Sw> treatments. These results suggest that the seaweed-based biostimulant may be a promising agronomic strategy to enhance sweet cherry chemical traits, especially with climate change. Further studies are needed exploring more fruit quality traits and more sweet cherry cultivars.

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Effects of the sowing date on the production of alkaloids in the seeds of three *Lupinus* species

Inês M. Valente[1,2*], André Monteiro[3], Carla Sousa[1], Margarida R. G. Maia[1], Ana R. J. Cabrita[1], Carlos Castro[3], Carla Miranda[3,4], António J. M. Fonseca[1], Henrique Trindade[3]

[1]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2]REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
[3]Centre for the Research and Technology Agro-Environmental and Biological Sciences (CITAB), Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801, Vila Real, Portugal
[4]Associated Laboratory for Green Chemistry (LAQV-REQUIMTE), University NOVA of Lisbon, Caparica, 2829-516 Lisbon, Portugal; Toxicology Research Unit (TOXRUN), University Institute of Health Sciences (IUCS), CESPU, CRL, 4585-116 Gandra, Portugal
**ines.valente@fc.up.pt*

Lupinus are plants of the Fabaceae family which seeds are of agricultural significance for their use as food or feed, in particular *L. albus* (white lupin), *L. angustifolius* (blue or narrow-leaf lupin), and *L. luteus* (yellow lupin). The seeds are especially rich in proteins and are an interesting alternative to soya beans, for example, as a non-animal protein source. Still, the lupins' seed can accumulate toxic amounts of alkaloids for humans and animals which will depend on their variety but also on the environmental and soil conditions [1].

In this work, the effects of the sowing location and dates on the alkaloids content in lupins' seeds of three species (*L. albus* Estoril, *L. angustifolius* Tango and *L. luteus* Cardiga) were evaluated. This study was carried out at two different experimental fields on the Northeast of Portugal, one at Vila Real and the other at Mirandela, simultaneously, with plants sown at 4 different dates between September and November 2018 using a randomized block design with plots of 10 m^2, 4 times replicated, resulting in 48 plots on each location. The samples were analysed by gas chromatography with mass spectrometry detection [2] and a total of 18 indole, piperidine and quinolizidine alkaloids were quantified. Data was analysed using the General Linear Model and Linear Regression Model procedures. The statistical models included the species, the local, the sowing date, and the interactions species x local, species x sowing date, and local x sowing date as fixed effects and the random residual error.

The results showed statistically significant differences ($p<0.05$) on the total alkaloids content with the *Lupinus* species, the sowing local and the interaction variety x local. In terms of individual alkaloids, the species showed differences on the levels of all the quantified alkaloids, although the local had only effect ($p<0.05$) on gramine, ammodendrine, lusitanine, lupinine, angustifoline, α-isolupanine, lupanine, 7-hydroxylupanine, 13-α-hydroxylupanine, and 13-α-angelolyoxylupanine. The sowing date and the interaction variety x sowing date were in general responsible for effects ($p<0.05$) on the content of quinolizidine alkaloids, rather than in the other chemical classes.

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Identificação e otimização da extração de compostos fenólicos de cascas de abóbora 'Butternut squash'

Maria G. Leichtweis[1,2], Adriana K. Molina[1,2], Carla Pereira[1,2,*], Maria Inês Dias[1,2], Márcio Carocho[1,2], M. Beatriz P.P. Oliveira[3], Isabel C.F.R. Ferreira[1], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Portugal
[3]REQUIMTE@LAQV, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal
*carlap@ipb.pt

Durante o processamento industrial da abóbora, grande parte da sua composição é descartada ou pouco aproveitada, nomeadamente cascas, sementes e fibras. No entanto, à semelhança de outros subprodutos da indústria alimentar, estes podem ser fontes promissoras de compostos de alto valor acrescentado [1]. Geralmente, estes compostos são moléculas provenientes do metabolismo secundário da planta, responsáveis por diversos mecanismos bioativos, o que justifica a sua recuperação para a obtenção de extratos bioativos. Entre os genótipos de abóbora mais utilizados na indústria alimentar para produção de polpa, o 'Butternut squash' é um dos mais representativos. No presente estudo, a casca deste genótipo foi avaliada quanto à sua composição em compostos fenólicos através de análise cromatográfica (HPLC/DAD-ESI/MS). Posteriormente, procedeu-se à otimização da extração de compostos fenólicos a partir deste subproduto, por maceração, recorrendo à metodologia de superfície de resposta (RSM). As variáveis independentes consideradas foram o tempo (t), a temperatura (T) e a concentração de etanol no solvente de extração (S), enquanto as variáveis dependentes monitorizadas foram o rendimento de extração (resíduo seco de extrato obtido) e a concentração em fenóis totais (através do método de Folin-Ciocalteu).

Quanto ao perfil fenólico, foram identificados cinco compostos, entre os quais quatro flavonoides. No entanto, o composto presente em maior concentração foi o flavan-3-ol (-)-epicatechin. Relativamente ao estudo de otimização da extração, a variável independente que mais afetou o rendimento de extração foi a proporção de etanol no solvente, seguida pelo tempo. A temperatura foi a variável que menos afetou o rendimento. No que respeita à concentração em fenóis totais, todas as variáveis tiveram alguma influência, sendo o tempo de extração a mais relevante. Verificou-se ainda que, no geral, concentrações mais elevadas de etanol levaram a menores rendimentos de extração (massa de resíduo seco); no entanto, permitiram obter maior concentração de compostos fenólicos, o que indica uma maior pureza dos extratos.

Estes resultados representam um importante contributo na descoberta de fontes sustentáveis de compostos de elevado valor acrescentado, como a casca de abóbora, um subproduto atualmente desperdiçado na indústria alimentar.

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Simultaneous determination of bisphenols, personal care products, and pesticide residues in fish species from Portuguese estuaries

Mateus H. Petrarca[1,*], Antía L. Cardama[1], Dhoone M. Sousa[1], Lúcia Guilhermino[2,3], Isa Marmelo[3,4,5], António Marques[3,4], Luís R. Vieira[2,3], José O. Fernandes[1], Sara C. Cunha[1]

[1]LAQV-REQUIMTE, Laboratory of Bromatology and Hydrology, Faculty of Pharmacy, University of Porto, Portugal
[2]ICBAS - School of Medicine and Biomedical Sciences, University of Porto, Department of Population Studies, Laboratory of Ecotoxicology and Ecology (ECOTOX), Portugal
[3]CIIMAR, Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Matosinhos, Portugal
[4]IPMA, Division of Aquaculture, Upgrading and Bioprospection (DivAV), Portuguese Institute for the Sea and Atmosphere, Lisbon, Portugal
[5]UCIBIO-REQUIMTE, Applied Molecular Biosciences Unit, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Caparica, Portugal
**petrarcamh@gmail.com*

Pollution of aquatic ecosystems is becoming increasingly prevalent at the global level, so environmental pollutants from several anthropogenic sources can accumulate in fish tissues. In addition to the negative effects on wildlife and biodiversity, bioaccumulation and biomagnification in the aquatic trophic chains can also affect human health through seafood consumption.

The main goal of this study was to evaluate the occurrence of a large number of compounds representing different categories of anthropogenic contaminants (thirty-six compounds: seven bisphenol analogues, four musk fragrances, four ultraviolet filters, and twenty-one pesticide residues) in the muscle of wild fish species from Douro and Tagus rivers estuaries, Portugal.

In total, 409 samples of the muscle of the species grey mullet (*Mugil cephalus*, n = 137), sea bass (*Dicentrarchus labrax*, n = 126), flounder (*Platichthys flesus*, n = 119), and barbus (*Barbus barbus*, n = 27), captured in the Douro and Tagus rivers estuaries in 2019 seasons (spring, summer, and autumn) and winter (2019-2020), were obtained from local fisheries. A sample preparation approach based on coupled QuEChERS and dispersive liquid-liquid microextraction (DLLME) techniques, with in situ acetylation of bisphenols, was used for the extraction of the target compounds [1]. The contents of the contaminants were determined by gas chromatography-mass spectrometry in selected ion monitoring (SIM) mode [1].

Suitable limits of detection and quantification were achieved, as well as adequate recoveries (70–120%), precision (RSD values < 20%), and linearity in matrix-matched calibration curves. Bisphenol A and bisphenol F were the main analogues found in the species. Among chemicals used in personal care products, galaxolide, tonalide, isoamyl 4-methoxycinnamate, and 2-ethylhexyl salicylate were the most often detected. About 60% of the samples contained residues of at least one pesticide, with alachlor, bifenthrin, *p,p′*-DDT, ethion, and prochloraz as the main compounds observed. Grey mullet was the species with a greater incidence of contaminants, mainly in those samples collected during the spring. The data obtained confirm the need for continuous monitoring of the presence of persistent contaminants in fish, taking into account the important adverse effects that they can cause on the health of consumers.

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Nutritional value of European seabass (*Dicentrarchus labrax*) muscle is affected by algae blend supplementation

Margarida R. G. Maia[1,*], Cátia S. C. Mota[1], Ana R. J. Cabrita[1], Helena Abreu[2], Joana Silva[3], Luísa M. P. Valente[4,5], António J. M. Fonseca[1]

[1]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portuga
[2]ALGAplus, PCI, Via do Conhecimento, 3830-352 Ílhavo, Portugal.
[3]ALLMICROALGAE – Natural Products, SA, R. 25 de Abril, 2445-413 Pataias, Portugal
[4]ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, R. Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[5]CIIMAR, Centro Interdisciplinar de Investigação Marinha e Ambiental, Terminal de Cruzeiros de Leixões, Av. General Norton de Matos, 4450-208 Matosinhos, Portugal.
**mrmaia@icbas.up.pt*

Algae, including micro- and macroalgae, are valuable and sustainable sources of nutrients, energy and compounds with bioactive activity, with potential to be used as functional aquafeed ingredients [1]. Although some studies have evaluated the dietary inclusion of individual microalgae or macroalgae species on muscle nutritional quality [2], the synergetic potential of a mixture of micro- and macroalgae species is almost non-existent. The present study aimed to fill this gap by assessing the effects of the dietary inclusion of a commercial algae blend (Algaessence®; Allmicroalgae and Algaplus, Portugal) composed of two macro- (*Ulva lactuca* and *Gracilaria gracilis*) and two microalgae (*Chlorella vulgaris* and *Nannochloropsis oceanica*) species on the muscle nutritional value and lipid quality of European seabass juveniles; an important marine species in the Mediterranean aquaculture.

Four iso-proteic, iso-lipidic and iso-energetic diets were fed to triplicate groups of juveniles (11.3 ± 2.7 g) for 12 weeks, differing on the algae blend supplementation levels: 0% (Algae0), 2% (Algae2), 4% (Algae4) and 6% (Algae 6). The algae blend was included in the diets at expense of wheat gluten and whole peas; fish meal and fish oil levels being kept constant. After 12 weeks, fish were weighted, and the right dorsal muscle collected from 9 animals per diet for proximate composition. Muscle fatty acids (FA) profile was determined by gas chromatography (GC-FID). Data were analyzed using the GLM procedure (SAS Institute), considering the fixed effect of diet and the random residual error.

Algae blend promoted the growth of European seabass juveniles and muscle lipid content ($P<0.001$) by nearly 1.7 fold with 6% inclusion. Muscle protein content was unaffected ($P=0.918$). The proportion of total monounsaturated FA increased ($P<0.001$) and total polyunsaturated FA (PUFA) decreased ($P<0.001$) with algae supplementation, while saturated FA kept similar ($P=0.442$). The dietary inclusion of algae blend gradually decreased the proportion of n-6 PUFA ($P<0.001$) and of n-3 PUFA ($P<0.001$) with algae supplementation. Of particular importance, the proportion of eicosapentaenoic acid (EPA) kept constant ($P=0.433$) while docosahexaenoic acid (DHA) decreased by 18.5% in fish fed Algae6 ($P<0.001$), most probably reflecting the absence of DHA in the algae blend. However, algae promoted the essential fatty acids (EPA + DHA) content (mg/g muscle; $P<0.001$) by nearly 43% in the dorsal muscle of European seabass juveniles, no differences being found among inclusion levels. Overall results unveil the potential of the algal blend as a natural modulator of the European seabass juveniles muscle nutritional value and lipid quality. Further studies are needed to assess the effects of long-term feeding, up to commercial size, as on organoleptic properties.

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On-farm dietary *Chlorella vulgaris* supplementation affects *Longissimus lumborum* fatty acid profile of finishing pigs

Ana R.J. Cabrita[1,*], Margarida R.G. Maia[1], Vitor Menino[2], João M. Almeida[3,4], Olga Moreira[3,4], António J. M. Fonseca[1]

[1]REQUIMTE, LAQV, ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[2]Valorgado, Agricultura e Pecuária, Estrada do Arçe 331, 2870-501 Sarilhos Grandes, Portugal.
[3]INIAV, Instituto Nacional de Investigação Agrária e Veterinária, Quinta da Fonte Boa, 2005-048 Vale de Santarém, Portugal.
[4]AL4AnimalS, CIISA, Centro de Investigação Interdisciplinar em Sanidade Animal, Faculdade de Medicina Veterinária, Universidade de Lisboa, Avenida da Universidade Técnica, 1300-477 Lisboa, Portugal.
**arcabrita@icbas.up.pt*

Pork meat represents an important animal protein source of the human diet particularly in western countries, being its impact on consumers' health a major concern of the industry. Typically, pork meat presents a poor source of omega-3 fatty acids, and a high omega-6 to omega-3 ratio. International health authorities recommend that the intake of omega-3 fatty acids should be 0.5–2% of total energy, and a omega-6 to omega-3 ratio between 5:1 and 10:1. The fortification of pork meat may constitute a strategy to increase the intake of omega-3 fatty acids, without changing the consumers behaviour. Although diet supplementation with microalgae has been shown to affect pork meat towards a healthier fatty acid profile [1, 2], evaluation at on-farm level is lacking. Therefore, the present study aimed to assess the effect of *Chlorella vulgaris* supplementation during the fattening and finishing periods on fatty acids profile of *Longissimus lumborum* of finishing pigs in a commercial farm.

A total of 120 pigs [50% castrated males:50% females; Pietrain x (Large White x Landrace)] were used. All animals were fed a commercial diet until 14 weeks of age, without the inclusion of microalgae. From that age until slaughter (at 25 weeks of age), pigs were distributed to one of two experimental diet groups: a fattening and finishing diet without (Control; n=60) or with the inclusion of 1% *C. vulgaris* (Algae; n=60), using the feeding management of the commercial farm (*ad libitum*; fattening diet until 20 weeks of age; finishing diet until slaughter). Animals were slaughtered in a commercial abattoir and *L. lumborum* samples obtained from each pig carcass, vacuum packed and stored at −20°C until analysis. Data were analysed using the MIXED procedure (SAS Institute), considering diet, gender, and the interaction between diet and gender as fixed effects, and the random residual error. Canonical discriminant analysis of the fatty acid profile was also performed to differentiate between Control and Algae diets.

Dietary supplementation with 1% *C. vulgaris* affected fatty acid profile but kept unaffected intramuscular fat (1.2%) and protein (24%) content. Regardless of the gender, supplementation with 1% *C. vulgaris* increased proportion of total polyunsaturated fatty acids (PUFA; $P < 0.001$) by 6.5%, including omega-3 fatty acids linolenic acid ($P < 0.001$), and eicosapentaenoic acid (EPA; $P = 0.009$), while kept unaffected total saturated fatty acids and docosahexaenoic acid (DHA) proportions. Overall results agree with earlier experimental studies and support *C. vulgaris* supplementation as a strategy to promote the unsaturation of pork meat. The potential of higher levels of algae supplementation towards more evident effects on fatty acids with known benefits for human health must be assessed.

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Recuperação de subprodutos da indústria alimentar para extração otimizada de compostos fenólicos

Maria G. Leichtweis[1,2], Adriana K. Molina[1,2], Carla Pereira[1,2,*], Márcio Carocho[1,2], Charikleia Vassilou[3], Spyridon A. Petropoulos[3], M. Beatriz P.P. Oliveira[4], Isabel C.F.R. Ferreira[1], Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Portugal
[3]Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Volos, Greece
[3]REQUIMTE@LAQV, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal
**carlap@ipb.pt*

Uma vertente muito importante da economia circular é a sustentabilidade. Alcançar metas como a redução do desperdício de alimentos e a minimização do consumo de energia e de produtos poluentes tem sido o foco de vários estudos recentes que visam a identificação da dinâmica de produção de bio-resíduos e subprodutos da indústria alimentar e a possibilidade de reaproveitamento dos mesmos [1]. Assim, o presente estudo visa a recuperação sustentável de subprodutos da indústria alimentar, nomeadamente de cascas de abóbora descartadas ao longo do processo de produção de polpas. Nesse sentido, as cascas de abóbora Grega 'Leuka Melitis' foram utilizadas para a obtenção de extratos ricos em compostos fenólicos através de duas técnicas de extração: maceração (M) e ultrassons (U). A otimização destes processos foi realizada recorrendo à metodologia de superfície de resposta (RSM) baseada no desenho experimental Box-Behnken, considerando como variáveis independentes o tempo de extração, a temperatura (MAC) ou potência (EAU) e a concentração de etanol no solvente, e como variáreis dependentes o rendimento de extração (resíduo seco) e a concentração de fenóis totais (método de Fólin-Ciocalteu).

Para ambas as respostas, o método alternativo de extração assistida por ultrassons demonstrou ser o mais vantajoso, especialmente no que respeita à concentração de compostos fenólicos totais, permitindo duplicar a concentração destes compostos, relativamente à maceração. Esta técnica permitiu ainda minimizar o tempo de extração, especialmente do que respeita ao rendimento, e diminuir a potência aplicada. De entre as três variáveis independentes analisadas, a concentração de etanol no solvente de extração foi a que apresentou maior influência em ambas as variáveis dependentes. No geral, concentrações mais elevadas de etanol levaram a rendimentos de extração inferiores, mas a teores mais elevados de compostos fenólicos nos extratos, revelando assim maior eficácia na recuperação de bioativos.

Os resultados apresentados corroboram a importância da recuperação de subprodutos da indústria alimentar para o desenvolvimento de extratos ricos em compostos bioativos, bem como a eficácia de técnicas alternativas de extração, permitindo a diminuição do desperdício de subprodutos e de energia.

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QUÍMICA AMBIENTAL Y SOSTENIBLE

Prospecção fitoquímica das folhas de *Dizygostemon riparius* (Plantaginaceae) morfotipo floral branco

Allan S. Godinho[1,*], Rogério M. Teles[1], Clenilma M. Brandão[1], Suzi M. Aires[1], Kiany S. B. Cavalcante[1]

[1]Programa de Pós-graduação em Química (PPGQ/IFMA), Instituto Federal de Educação, Ciência e Tecnologia do Maranhão – IFMA, Campus São Luís Monte Castelo. Avenida Getúlio Vargas, n°04, Monte Castelo, 65030-005, São Luís, Brasil
*allan.sampaio@acad.ifma.edu.br

As plantas possuem inúmeros compostos naturais que ganharam notoriedade nas últimas décadas por suas atividades biológicas e propriedades biodegradáveis, menos prejudiciais ao homem e ao ambiente. A relação entre a bioatividade e os fitoconstituintes das plantas são um dos principais fatores dessa bioatividade. Taninos, alcalóides, compostos fenólicos e flavonóides são classes de compostos orgânicos com ação biológica ativa documentada na literatura, como agentes antibacterianos, antifúngicos e anticancerígenas[1].

Em razão dessas propriedades, o estudo tem como objetivo investigar a composição fitoquímica das folhas de *Dizygostemon riparius* (Plantaginaceae) morfotipo flor branca, espécie aromática identificada em 2019 [2] e coletada na região do Cerrado maranhense, Brasil (3°19’25.550” S / 43°31’0.923” W), local do seu primeiro registro [3]. Para o estudo dos metabólitos secundários de *D. riparius,* foi realizado a prospecção fitoquímica de Matos (2009) [4], com modificações. Para realização do estudo, foi utilizado os extratos brutos acetato de etila, metanólico e aquoso de *D. riparius*. As reações químicas de caracterização foram classificadas em abundantes, moderado, pouco, suspeito ou ausente.

Os resultados da prospecção fitoquímica indicam presença de expressivos compostos nos extratos foliares de *D. riparius.* Os resultados apresentados são similares aos estudos da espécie com o morfotipo lilás [3] e outras espécies da família Plantaginaceae, os quais indicam similaridade dentro dessa família quando identificaram a presença de flavonoides, alcaloides, triterpenoides e saponinas [5;6,7]. Substâncias químicas, constituídas por hidroxila e anel aromático, comumente encontradas em espécies vegetais, as quais conferem proteção contra microrganismos e insetos [8]. Além disso, pode-se observar maior presença de compostos fenólicos, como os flavonoides, fitoquímicos com potencial antioxidante e antibacteriano. Saponinas e alcalóides também foram observados, fitoquímicos que apresentam atividade biológica [1]. Dessa forma, *D. Riparius* apresenta potencial para investigação futura dessas atividades visto a presença de importantes classes químicas nesta planta nativa do Brasil.

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Evaluación de la degradación del benzo(a)pireno por microalgas y sus extractos enzimáticos por medio de metodología SPE-HPLC

M.P. García de Llasera[1,*], **Gerardo Peralta Marín**[2]

[1]Universidad Nacional Autónoma de México (UNAM), Av. Universidad 3000. 04510, CDMX, México
[2]Universidad Nacional Autónoma de México (UNAM), Av. Universidad 3000. 04510, CDMX, México
**pgcllas@unam.mx*

La contaminación del agua por hidrocarburos aromáticos policíclicos (PAHs en inglés) es un tema que requiere de mucha atención en la actualidad porque son contaminantes peligrosos y ampliamente distribuidos en el planeta. Los PAHs están constituidos por dos o más anillos aromáticos, lo que los hace hidrofóbicos y altamente persistentes en el ambiente [1, 2]. El benzo(a)pireno (BaP) que contiene cinco anillos, es carcinogénico y se ha encontrado en agua, suelos y atmósfera [3]. La remediación por los PAHs puede hacerse mediante métodos biológicos usando bacterias, hongos o microalgas [4-5], por lo que sus enzimas juegan un papel muy importante en la biorremediación [6].

En el presente trabajo se evaluó la degradación del BaP en cultivos con medio líquido Bristol de la microalga *Selenastrum capricornutum*, y en extractos crudos obtenidos por lisis ultrasónica de su biomasa pre-expuesta (activada) al contaminante [7]. Se realizaron ensayos de exposición al BaP a 22, 28 y 34° C durante 3 h en los cultivos y en los extractos inmovilizados en cuentas de alginato sumergidas en 15 mL de buffer TRIS pH 7. El análisis de BaP y su metabolito, el 4,5-dihidrodiol BaP, se efectuó con metodología analítica basada en extracción en fase sólida (SPE en inglés) y cromatografía de líquidos de alta resolución (HPLC en inglés) con detección UV y de fluorescencia.

Se observó que la degradación aumentaba con la temperatura: 19, 46 y 58% en los cultivos con células microalgales, y 48, 53, 60% en los extractos enzimáticos inmovilizados. Se observaron valores significativamente diferentes entre la degradación en cultivos y en extractos inmovilizados a 22 °C, pero no hubo diferencias significativas entre éstos a 28 y 34 °C. La degradación fue menor en células a 22 °C probablemente porque la célula presenta metabolismo más lento a la temperatura baja. Por otro lado, el extracto no inmovilizado conteniendo a la enzima libre también se expuso al BaP, presentando 36, 39 y 40 % degradación. La enzima inmovilizada presentó eficiencia degradativa mayor que la de la enzima libre debido a que se encuentra dentro de la cuenta, en un medio protegido de las condiciones externas. Por otra parte, los ensayos de exposición a 28 °C se realizaron también con incubación de 6 h, encontrándose 57 y 64% de degradación para cultivos con células y extractos con enzimas inmovilizadas, respectivamente. La biodegradación fue corroborada por la detección del metabolito 4,5 dBaP en estos ensayos de exposición. Cabe destacar que la enzima degradadora aún no está identificada, pero la desaparición del BaP en el tiempo y la aparición del metabolito demostraron que los extractos contenían a la enzima con buena funcionalidad. Los resultados son prometedores para la utilización de la enzima microalgal para efectos de biorremediación.

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Ecotoxicity evaluation of treated wastewaters using *Daphnia magna* and *Raphidocelis subcapitata*

Maria Luz Maia[1,*], Ângela Guedes[1], Ana Rita Alves[1], Andreia Daniela Silva[1], Inês Baptista[2], Sónia Figueiredo[1], Valentina F. Domingues[1], Cristina Delerue-Matos[1]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, 4249-015 Porto, Portugal
[2]Wedotech, Lda, Rua do Seixal nº108, 4000-521 Porto, Portugal
**mariadaluz.maia@gmail.com*

Micropollutants, such as pharmaceuticals have been threatening aquatic ecosystems in recent years. To eliminate these emerging pollutants from wastewaters efficiently, terciary treatment is required to refine the secondary treatment. It is essential that, in addition to evaluating their efficiency, ecotoxicity tests are carried out to assess the toxicity level after treatment. One of the most widely used biological assays are acute tests with microcrustaceans, e.g. *Daphnia magna* [1], and chronic tests with microalgae, e.g. *Raphidocelis subcapitata*, being both standard test organisms in ecotoxicity.

In the present work, two trophic levels, microalgae and microcrustaceans were used to analyze the ecotoxicity of four different treated wastewaters, one after secondary treatment and three others after tertiary treatment: ultraviolet radiation (UV), ozonation (OZ) and ultrafiltration (UF). For all the ecotoxicity tests standard guidelines were employed [2-4]. Briefly, the daphnids were obtained from the incubation of dormant eggs, for 72 h prior to the tests, at 20° C with continuous light. Neonates less than 24 h old, were pre-fed with a suspension of spirulina 2 h before the tests. After that, the organisms were placed on a multicell test plate. The control and each sample dilution were performed in quadruplicate. Five dilutions of each water effluent were conducted (30%, 45%, 60%, 75% and 100%). The number of dead daphnids was registered after 24 h and 48 h. In the case of microalgae, the growth medium was prepared according to the OECD guideline [4] and then solutions with different concentrations of the effluent (5%, 10%, 20%, 40% and 80%) were tested, in quadruplicate. The microalga *R. subcapitata* was exposed to the effluent for 72 h. The response was evaluated as a function of the exposure concentration and compared to the growth of the control cultures to estimate the algal growth inhibition.

The results of the tests concerning secondary effluent and tertiary effluent with UV and UF treatment, showed no significant mortality of daphnids at the end of the 48 h and, therefore, it was not possible to determine the concentration that affects 50% of the organism population (EC50). On the other hand, in the test concerning the effluent with tertiary treatment by OZ, there was obtained mortality of the test organisms, and an EC50 of 86% was obtained. In the case of the microalga, an EC50 of 11% was obtained after the secondary treatment, and after the tertiary treatments the following EC50 values were estimated, 7% for UV, 7% for UF and 35% for OZ. The inhibition growth did not increase proportionally with the wastewater concentration in the assay, due to the effect of nutrient concentration increase, which favors the algal growth. These results suggest that the toxicity of the effluent is dependent both on the organism (trophic level) and on the treatment applied.

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Microplastics in Portuguese agricultural soil: identification by Raman Spectroscopy

Diana Rede[1,2], Freddy Mbene[1,3], Rui Vilarinho[4,5], Joaquim Agostinho Moreira[4,5] ,Cristina Delerue-Matos[1], Virgínia Cruz Fernandes[1,*]

[1]REQUIMTE/LAQV, Porto School of Engineering, Polytechnic Institute of Porto, Porto, Portugal
[2]Department of Chemistry, Faculty of Sciences of the University of Porto, Porto, Portugal
[3]IUT of Orsay, University of Paris Saclay, France
[4]Department of Physics and Astronomy, Faculty of Sciences of the University of Porto, Porto, Portugal
[5]IFIMUP—Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Faculty of Sciences of the University of Porto, Porto, Portugal
**virginiacruz@graq.isep.ipp.pt*

The ubiquity of microplastics (MPs) has been recognized as a major threat to the environmental compartments [1]. Soil is identified as the main reservoir of MPs, and among the possible sources of contamination, agriculture can be highlighted as a significant contributor. In fact, agricultural practices end up being both victims and sources of MPs [1]. The presence of MPs in agroecosystems has raised major concerns, both concerning impacts on soil quality and biota and human health. Yet, the possible adverse effects remain poorly understood, largely due to, the lack of standard methods for extracting and analysing MPs [2,3]. This study was conceived to optimize the extraction procedure of MPs from soil proposed in the literature [4–6] using pristine MPs of different polymers (low density polyethylene (LDPE), < 300 µm powder; polystyrene (PS), 3-5 mm spheres; ethylene vinyl acetate copolymer (EVA), 3-5 mm; polyvinyl chloride (PVC), < 250 µm powder; polypropylene (PP), < 5 mm spheres; and Nylon 6.6, 5-50 µm powder) and Lufa 2.2 certified soil (Lufa Speyer).

The overall procedure was conducted in 4 steps: i) oxidation of the organic matter; ii) flotation of the microplastics in solution; iii) filtration of the supernatant; and iv) identification of the recovered microplastics by Raman spectroscopy. Firstly, the pre-dried soil was sieved on a column using 3 pore openings (1 mm, 100 µm, and 40 µm), obtaining 4 fractions, these being > 1 mm; [100 µm, 1 mm]; [40, 100 µm]; and <40 µm. The fraction > 1 mm was spiked with MPs and mixed with 20 mL of hydrogen peroxide solution (30%) to oxidize the organic matter. Then, flotation was performed by testing two different solutions: sodium chloride (1.2 g cm^{-3}) (for the 6 polymers) and 96% (v/v) ethanol (for LDPE and PS). At this stage, 20 mL of flotation solution was added and the top layer was vacuum filtered. Next, 3 mL of hydrogen peroxide was added to the filter to remove the remaining organic matter. A second filtration was performed, and the filter was dried at 40 °C for 1 hour. The separation efficiency of the procedure was evaluated by calculating the percentage recovery. The filter was studied using Raman spectroscopy (spectral range between 100 - 4000 cm^{-1}) identifying the recovered MPs. The procedure was repeated for each of the 6 MPs.

The obtained results show that the procedure with sodium chloride allowed to obtain the following recoveries (%): Nylon 6.6 (14%) < PVC (40%) < EVA (62%) < LDPE (76.5%) < PP and PS (100%). The recoveries below 75% obtained for Nylon 6.6 and PVC (14% and 40%, respectively) are due to the fact that these polymers have a higher density than the saline solution. As for the EVA-MPs, the recovery obtained can be explained by the damage on the surface of the particles, and visible to the naked eye, caused by the oxidation with hydrogen peroxide. Moreover, the use of ethanol in the flotation of LDPE and PS did not produce improvements in the process. Regarding Raman spectroscopy, a comparison of the spectra obtained with the literature allowed confirmation that the recovered materials were the MPs under study. For example, the PS spectrum showed a prominent peak at 1000 cm^{-1}, peaks of lower intensity in the interval 1450-1500 cm^{-1} and another prominent peak at 1600 cm^{-1}, which corresponds to aromatic ring chain vibrations. It can be concluded that the best protocol to isolate MPs, namely PS and PP was flotation with sodium chloride. However, further studies are needed to develop a protocol that allows the simultaneous extraction of MPs from different polymers.

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Carbon Materials as Renewable Catalysts for CO_2 Addition to Epoxides

<u>Inês G. Cruz</u>[1,*], João M. Gil[2], Fábio S. Ferreira[3], Mariette M. Pereira[1], Rui M. B. Carrilho[1]

[1]CQC, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
[2]CFisUC, Department of Physics, University of Coimbra, Rua Larga, 3004-516 Coimbra, Portugal [3]SEG-
CEMMPRE, Department of Mechanical Engineering, University of Coimbra, Rua Luís Reis Santos,
3030-788 Coimbra, Portugal
**inesgcruz682@gmail.com*

Climate changes are one of the major problems nowadays, largely due to the high emission of greenhouse gases into the atmosphere. One of the most abundant greenhouse gases is carbon dioxide (CO_2), which can be captured, used or stored in order to decrease its concentration in the atmosphere.[1,2] Carbon materials, namely those obtained from renewable sources like wood bark, are capable to accomplish these three promising approaches for the mitigation of CO_2 emissions.[3]

In this work, we present the studies of the physical-chemical properties of two different carbon materials (vegetable charcoal and activated charcoal) in their initial formulas. Their porous structure was studied by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS), which confirmed that activated charcoal, obtained from thermal/chemical treatment of vegetable charcoal, has a higher porosity. In addition, CO_2 adsorption/desorption isotherms studies[4] have showed that activated charcoal stands out with a maximum of 6.33 mmol/g at room temperature.

Furthermore, the materials were evaluated as heterogeneous catalysts in CO_2 cycloaddition reactions to epoxides, with activated charcoal standing out as the most efficient, with a 35 % conversion in 24h, without the use of any co-catalyst, and 100 % selectivity for the formation of cyclic carbonates (Fig. 1).

Fig.1. Carbon materials with CO_2 adsorption properties as catalysts for reactions of cycloaddition of CO_2 to epoxides

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Plantas aquáticas como bioindicadores da poluição de sistemas estuarinos por metais pesados

Cristina Morais Couto[1,2*], Agostinho A. Almeida[2], Cláudia Ribeiro[1,3]

[1]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, CESPU, CRL, Gandra, Portugal
[2]LAQV/REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3]Interdisciplinary Centre of Marine and Environmental Research (CIIMAR/CIMAR), Terminal de Cruzeiros do Porto de Leixões, University of Porto, 4050-208 Matosinhos, Portugal
**cristina.couto@iucs.cespu.pt*

Os sistemas aquáticos, nomeadamente os estuarinos, estão sujeitos a fortes pressões antropogénicas, em particular quando inseridos em zonas urbanas. Sendo estes sistemas dinâmicos, os estudos de monitorização devem integrar diferentes compartimentos abióticos (p.e. água, solos) e bióticos para uma correcta avaliação de possíveis perturbações. O recurso a plantas aquáticas, nomeadamente macrófitas tem sido usado como uma ferramenta valiosa na monitorização de poluição por metais [1].

Neste estudo utilizaram-se macrófitas autóctones, *Veronica anagallis-aquatica* e *Cakile maritima*, para avaliar a possível bioacumulação de vários metais pesados, em dois importantes estuários do norte de Portugal [2, 3]. Estes estuários estão sujeitos a elevada pressão antropogénica, devido à descarga de resíduos de origem urbana, industrial e agrícola.

As determinações de cobre, crómio, chumbo e zinco foram efetuadas por ICP-MS após digestão em microondas, de espécimes colhidas nos dois estuários, assim como água e sedimentos do mesmo ponto de colheita. Foram encontradas diferenças nos teores dos metais analisados, sendo o Zn o metal encontrado em maior concentração, seguido do Cu, e do Cr ou Pb dependendo do estuário e da planta estudada. Não foi encontrada uma correlação positiva entre os teores de metais pesados nas plantas e água; no entanto foi observada uma correlação positiva para o Cu, Pb e Zn entre as plantas e os sedimentos.

Com os dados obtidos procedeu-se à determinação do Factor de Bioacumulação e do Factor de Translocação que demonstraram que estas plantas podem contribuir para a imobilização de metais pesados, sendo ferramentas úteis como bioindicadores da poluição por metais em meios aquáticos.

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Degradación de láminas conductoras transparentes de óxido de indio dopado con estaño (ITO)

B. Asenjo. [1*]

[1].CIEMAT, Department. of Energy, Avda. Complutense, 40, 28040 Madrid, Spain
** mbegona.asenjo@ciemat.es, Tel.: +34 913466101; fax: +34 9134660372*

A lo largo del tiempo, una gran multitud de los módulos fotovoltaicos sufren degradación durante su vida útil. Este hecho produce una pérdida de la potencia dada por el módulo, y, en los peores casos, puede llegar a suponer la rotura e inutilidad de éste [1].

Una de las causas es la degradación de los materiales que componen la estructura de las células y del módulo solar [2].

Con el fin de estudiar la influencia que pueden tener las condiciones climáticas a las que estén expuestos los módulos en sus propiedades ópticas, se han llevado a cabo unos ensayos de vida acelerada de radiación ultravioleta, de la lámina de ITO (oxido de indio dopado con estaño), que forma parte de la estructura de la célula solar. Este material es el óxido conductor (TCO), utilizado como electrodo transparente que es la capa activa encargada de absorber la luz incidente en el dispositivo. El procedimiento experimental ha consistido en la medición de las propiedades ópticas de varias muestras de vidrio primero, y a continuación del dispositivo ITO/vidrio. Se pretende estudiar la degradación que sufren las diferentes muestras en función del tiempo de exposición. El ensayo de UV se ha realizado siguiendo las indicaciones recogidas en la norma UV DE UNE-EN 61215, La luz ultravioleta es la radiación electromagnética emitida en el rango de longitudes de onda entre los 200 y los 400 nm por ello en el ensayo se han utilizado dos lámparas OSRAM Ultra Vitalux, de 300W cada una, y se han definido las siguientes correlaciones:

- Relación UVA/W = 13.6
- Relación UVB/W = 3.0

La duración total del ensayo ha sido de 300 horas de exposición, manteniendo una temperatura en el interior de la cámara entre 55 y 60ºC. Para el control de la temperatura durante el ensayo tanto las muestras como las lámparas, se han colocado en una cámara termostatizada.

Se han realizado medidas de las propiedades ópticas de las muestras cada 100 horas de ensayo y se ha llevado a cabo la caracterización de las láminas para determinar el porcentaje de degradación que pueden sufrir estos materiales y determinar así su vida útil.

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Characterization TiO_2 chemically deposited on ITO substrate for solar cells.

B. Asenjo. [1,*], **J.J. Gandía.**[1]

1.CIEMAT, Department. of Energy, Avda. Complutense, 40, 28040 Madrid, Spain
* *mbegona.asenjo@ciemat.es, Tel.: +34 913466101; fax: +34 913466037*

Titanium oxide (TiO_2) thin films has been investigated by many researcher because have many applications, are used in electronic circuits, solar cells, anti-bacterial applications, photocatalysis, etc. This material has large band gap, 3.2 eV with electrical and optical properties for three different crystalline structure: rutile, anastase and brookite.

TiO_2 have been prepared by several methods: pulse laser deposition [1], chemical bath deposition [2], spray pyrolysis [3].etc.

This study is based on the preparation of titanium oxide (TiO_2) films by sol-gel method, deposited on ITO/glass substrate (tin doped indium oxide/glass) through the spin coating technique for photovoltaic applications.

Different films have been obtained depending on the thickness deposited on the ITO/glass (A sample: 40 nm, B sample: 70 nm and C sample; 90 nm) and titanium (IV) butoxide was used as precursor.

The optical, structure, and electrical conductivity characteristics of titanium oxide samples have been analyzed as a function of preparation conditions.

Through transmittance measurements in the UV-Vis range, it was observed that TiO_2 incorporation varies the transmittance of the ITO substrate. Being in the films with greater thickness the one that shows a greater reduction of the transmittance (52%) compared to ITO/substrate without TiO2 (82%).

There are differences between the energy gap values of the films, ranging from 2.57 eV to 3. 3 eV. As the thickness increase for the same concentration of titanium precursor, its value decreases.

The crystalline phase for the deposited films is anastase. Optical microscopic (OM) analysis show the surface morpholy. (Fig. 1)

The TiO_2 coating on the ITO substrate is homogeneous in the deposited film with a thickness of 90 nm.

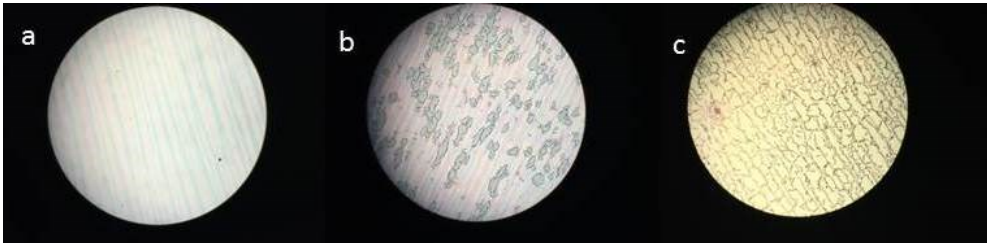

Fig.1. OM images of samples: a) 40nm b) 70 nm and c) 90nm

The TiO_2/ ITO films can be used in the fabrication of non toxic solar cells.

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Supervised classification combined with genetic algorithm variable selection for microplastics measured by infrared spectrometry

Borja Ferreiro [1,*], Jose M. Andrade [1], Riccardo Leardi[2], Emanuele Farinini[2]

[1] Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA),
Universidade da Coruña, 15071 A Coruña, Spain
[2] Department of Pharmaceutical and Food Chemistry and Technology, Faculty of Pharmacy,
University of Genoa, Genoa, Italy
** Corresponding author: fax: +34-981-167065; borja.fferreiro@udc.es*

Plastic pollution is one of the most ubiquitous, insidious contaminants in the environment, and causes serious concerns in Society. Most applications of plastic products are single-use, like bags or food packaging. This, combined with long times of polymer decomposition and the enormous quantities produced (376 million tonnes in 2020 [1]) results in a high presence and permanence of polymer fragments in the environment, especially in seas and oceans. To mitigate this problem, it is necessary to get detailed and precise information on how the polymers are introduced in the environment, their loads in the spillages, how they distribute, how they behave in the natural ecosystems (including their sinks), etc. All these evaluations require a fundamental step, which is the identification of the main polymer that constitutes the plastic fragment.

Hence, a new method of polymer identification was developed based on infrared spectroscopy and its combination with several multivariate chemometric methods. Variable reduction by means of Genetic Algorithms was a main preliminary step as a way to get rid of the big amount of irrelevant information (from different sources) in the spectra that blur polymer identification. Our final objective was to identify the main polymer of the fragments independently from their aging.

Nine types of polymers, pristine and artificially aged, in two presentations: pellets and powders, were used to develop chemometric models using *k*-Nearest Neighbours (KNN), Linear Discriminant Analysis (LDA) and Quadratic Discriminant Analysis (QDA). The spectroscopic measurements were performed in microreflectance and attenuated total reflectance (ATR) modes. The models were validated using a subset of the artificially aged samples (not used for calibration), as well as a suite of field samples from several Mediterranean beaches [4]. The best results were obtained with KNN models for ATR-measured spectra, with a percentage of correct predictions over 80 %.

Acknowledgements

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Study of carbon matrix supported on carbon fiber as gas diffusion electrode for electrogeneration of oxidants species using a flow-by reactor

Taynara O. Silva[1,2*], Marcos R. V. Lanza[1], Manuel A. R. Rodrigo[2]

[1]Chemistry Institute of São Carlos – University of São Paulo, Av. Trab. São Carlense, n°400, São Carlos, Brazil.
[2]Chemical Engineering Department, University of Castilla-La Mancha, C. Altagracia, n° 50, Ciudad Real, Spain
taynaraos1994@usp.br

One of the main challenges of environmental studies is the removal of pollutants, among them, are: pesticides, plasticizers, antibiotics, etc., [1,2] In this context, studies addressing alternative forms of degradation have been studied, Advanced Oxidative Processes (AOPs) are one of the highlights, having the hydroxyl radical (OH•) as the principal oxidant species [2,3]. Hydrogen peroxide (H_2O_2) is one of the most used reagents in the advanced oxidated process (AOPs) for being the main precursor of OH•.

This oxidant is formed by the oxygen reduction reaction (ORR), where one of the limitations of this reaction is the solubilization of oxygen in the reaction medium [1]. Thus, gas diffusion electrode (GDE) of carbon matrix appears to overcome this problem due to its triple interface. For this reason, Studies seeking to scale up the electroproduction of hydrogen peroxide in reactors have been growing.

In this work, the gold was to study current density conditions for the electrogeneration of hydrogen peroxide in a flow reactor, using different counter electrodes and evaluate their influence on the reaction. The currents density's studies were: 25 $mAcm^2$, 50 $mAcm^2$, 75 $mAcm^2$ and 100 $mAcm^2$. In an acid medium Na_2SO_4 0,5M; pH 2.5 adjusted with H_2SO_4 1M using a volume of 1 L, and flow of O_2 50 mL h^{-1}.

As a result, the system was capable of electrogenerated H_2O_2. At a current density of 100 $mAcm^2$ had a total peroxide value generated after 90 min of 434.0 mg L^{-1}. This was the current density with the highest H_2O_2 value among those studied. When applying the other currents of 25 $mAcm^2$, 50 $mAcm^2$, and 75 $mAcm^2$ the values of peroxide electrogenerated was 143.51 mg L^{-1}, 229.7 mg L^{-1} e 274.4 mg L^{-1}, respectively.

Calculations of current efficiency and energy consumption were also performed to evaluate the performance of the material and the reactor.

Acknowledgments
University of São Paulo, Chemistry Institute of São Carlos University of Castilla - La Mancha, Chemical Engineering Department, FAPESP Process: 2019/08701-4; 2017/10118-0; 2022/07227-0.

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La importancia de la gestión del excedente textil en el nuevo marco de la Ley de Residuos

Santiago Urréjola-Madriñán[1, *], **Rosa Devesa-Rey**[1, *], **José Luis Varela-Alende**[2], **Lorena González-Gil**[1],

[1] Centro Universitario de la Defensa en la Escuela Naval Militar, Universidad de Vigo, Plaza de España 2, 36920 Marín, Pontevedra, España
[2] Letrado de la Administración de Justicia Sustituto
**urrejola@cud.uvigo.es*

Diariamente se producen miles de toneladas de productos textiles, de difícil eliminación y que en el medio ambiente pueden resultar notablemente tóxicos. La industria textil es, de hecho, la cuarta en importancia en cuanto a la presión ejercida sobre el medioambiente después de la alimentaria, los desechos producidos en los hogares y los producidos en el transporte en todo el mundo [1]. En España solo se reciclan el 12,16% de los residuos creados por este sector lo que significa que más de 800.000 toneladas de estos productos acaban en los vertederos del Estado anualmente [2]. Aproximadamente el 63% de la materia prima de los productos textiles procede de derivados del petróleo [3] lo que implica asimismo una generación de 1.715 Mt de emisiones de CO2eq, el consumo de unos 80 billones de metros cúbicos de agua y la generación de aproximadamente 95 Tm de residuos textiles. Además, desde una perspectiva de calentamiento global, debe tenerse en cuenta que la problemática de dichos residuos no afecta sólo a su producción, sino que hay que tener en cuenta todos los recursos utilizados para su fabricación, lo que conlleva una masiva producción de gases nocivos para la atmósfera acrecentando así el efecto invernadero y la destrucción de la capa de ozono. Es indudable que el volumen de residuos producidos anualmente ejerce una presión insostenible sobre el medioambiente y gran parte de los esfuerzos en la actualidad se dirigen hacia la mitigación de la producción de estos residuos mediante su recogida y tratamiento selectivo. Más aún, es necesario trabajar en el desarrollo de tecnologías que faciliten su reciclado o revalorización, contribuyendo a una economía circular mucho más sostenible.

La nueva Ley 7/2022, de Residuos y Suelos Contaminados introduce importantes modificaciones en cuanto a los residuos textiles, un sector que tradicionalmente ha recibido menos atención en cuanto al volumen y gestión de restos producidos. La industria textil es, de hecho, la cuarta más contaminante en volumen de residuos y, además, se ha visto incrementada por la práctica social del empleo de moda rápida. Por lo anteriormente mencionado, cobra especial importancia la Directiva Europea ((EU) 2018/851) por la que se modifica la Directiva 2008/98/CE sobre los residuos. Esta nueva Directiva obliga a los Estados Miembros a la recogida selectiva de residuos textiles antes del 1 de enero de 2025, y al establecimiento de unos objetivos relativos a la preparación para la reutilización y al reciclado de estos residuos. Esto supondrá un impacto para toda la cadena de valor textil pues será necesario que las empresas empiecen a diseñar y preparar sus productos para contener material reciclado y para permitir su reciclaje. Las nuevas tendencias en gestión de desechables textiles impulsan el aumento de la concienciación ciudadana sobre las prácticas de consumo, así como la corresponsabilidad de productores y usuarios. La gestión de restos textiles, cuyo principal destino es la economía social, habrá de impulsar las tecnologías de valorización de los excedentes para reintroducir dichos materiales en el proceso de consumo, favoreciendo de esta forma la economía circular y la sostenibilidad.

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AMB47

Zn-Doped Carbon Catalysts Highly Efficient for Benzodiazepine Synthesis: Tires Valorization

Antonio J. López Peinado[1], Marina Godino-Ojer[2], I. Matos[3]*, María Bernardo[3], Isabel M. Fonseca[3], Elena Pérez-Mayoral[1]*

[1] Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Facultad de Ciencias, Urbanización Monte Rozas, Avda. Esparta s/n Ctra. de Las Rozas al Escorial Km 5, 528232 Las Rozas, Madrid, España
[2] Facultad de Ciencias Experimentales, Universidad Francisco de Vitoria, UFV, Ctra. Pozuelo-Majadahonda km 1.800, 28223 Pozuelo de Alarcón, Madrid, España
[3] LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
alopez@ccia.uned.es

Spent tires constitute a serious environmental problem worldwide. High carbon content of this type of waste makes feasible to transform them into valuable compounds such as activated carbons (ACs) [1].

The goal of this paper is to synthesize and characterize a new family of carbonaceous materials, prepared from used tires, able to efficiently catalyse the synthesis of benzodiazepines, one of the most pharmacologically relevant nitrogenous heterocycles showing a great variety of biological activities, from differently substituted *o*-phenylendiamines and acetone [2].

Carbon-based materials herein reported have been synthesized by pyrolysis of tires (CPN) followed by activation with H_3PO_4 or CO_2. The synthesized catalysts are a family of thermally stable activated carbons with a high content of C and S. Activation with H_3PO_4 increased the acidity of the catalyst surface, with the formation of P-O-Si, Si-O-Si or P-O-P species. CPN is presented as a macroporous material with a high content of Zn and Si, elements present in the tire manufacturing process.

All the investigated catalysts were tested in the synthesis of benzodiazepine giving rise to high conversions of *o*-phenylendiamine. CPN_H_3PO_4 turned out to be the most selective catalyst leading to high conversions of *o*-phenylendiamine (95%) and a selectivity to benzodiazepine close to at 90% (4h). The higher acidity of CPN_ H_3PO_4 seems to be decisive in the observed selectivity. In addition, we also carried out a theoretical study, by computational methods, analysing the last step of the reaction comprising the cyclization step. The theoretical results strongly suggest that the most probable active specie could consist of phosphorylated function containing Zn (Model b: $ZnC_6H_5\text{-}OP{=}O(O)_2$) instead Brönsted acid sites in $C_6H_5\text{-}OP{=}O(OH)_2$ (Model A), both as reduced models simulating the possible active catalytic sites. Accordingly, the HOMO-LUMO gap for the corresponding reactant complexes (Model b) is notably lower than that for Model a but also for the reaction in absence of any catalyst. It is also supported by the increase of electrophility of carbon acceptor (C=N moiety) involved in cyclization step (Fig.1).

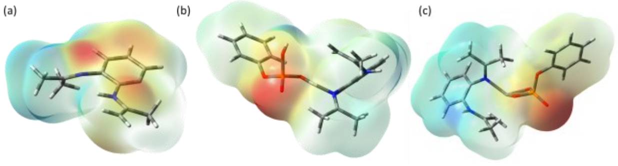

Fig.1. Electron density maps from SCF in the reactive complexes of the cyclization step in the synthesis of benzodiazepines without catalyst (a), in the presence of Model a (b) and Model b (c).

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Quinolines synthesis promoted by carbon catalysts from polyethylene terephthalate (PET). Wastes valorisation

Antonio J. López-Peinado[1], **Marina Godino-Ojer**[2], **Vanessa Ripoll Morales**[2], **Luisa M. Pastrana-Martínez**[3], **Francisco J. Maldonado-Hódar**[3], **Elena Pérez-Mayoral**[1]*

[1]Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Urbanización Monte Rozas, Avenida Esparta s/n, Ctra. de Las Rozas al Escorial Km 5, 28232 Las Rozas-Madrid, Spain
[2]Facultad de Ciencias Experimentales, Universidad Francisco de Vitoria, UFV, Ctra. Pozuelo-Majadahonda km 1.800, 28223 Pozuelo de Alarcón, Madrid, Spain
[3] NanoTech-Nanomaterials and Sustainable Chemical Technologies. Faculty of Sciences. University of Granada. Avda. Fuente Nueva s/n, 18071, Granada. Spain
alopez@ccia.uned.es

Nowadays, plastic is one of the main raw materials that supports the development of modern societies. It is produced from non-renewable resources and its use entails environmental concerns, such as ocean water pollution and compromising food security [1]. At this regard, scientific community is seeking new alternatives for converting plastic wastes into high-value products [2]. In this context, wastes with high polyethylene terephthalate (PET) content were used for designing carbon catalysts that can be employed in the synthesis of compounds with therapeutic activity [3].

The present work aims to assess the activity of different carbon basic materials derived from PET wastes [4] on catalytic synthesis of quinolines. Carbon materials were prepared plastic wastes, K_2CO_3 and urea adapting the experimental protocol previously reported by Arenillas et al. [5]. Four different homogeneous PET/K/Urea mixtures were prepared by mixing the components at varying the PET/K/urea ratio: 1:0.5:0, 1:0.5:0.25, 1:0.5:0.5 and 1:0.5:1, respectively. The composition and the textural characteristics of the samples were determined from N_2 adsorption/desorption isotherms, thermogravimetric, elemental analyses and FT-IR spectroscopy. The catalysts under study present low specific surface area ranging 10-20 m^2/g. The FTIR-ATR spectra of samples show characteristic bands of nitrogen corresponding to single and double carbon-nitrogen bonds. Furthermore, most active catalysts also showed a band associated to C-OH groups.

Catalytic activity was performed in the Friedländer condensation from 2-amino-5-chlorobenzaldehyde (0.5 mmol) and ethyl acetoacetate (5 mmol), under solvent-free conditions, at 30 ºC, using 25 mg of catalyst. Samples were collected at different times and diluted with dichloromethane. Afterwards, the catalyst was separated by filtration and the solvent evaporated in vacuo. Samples were analysed by ^1H NMR spectroscopy. All investigated carbon catalysts were active in the reaction yielding high conversion values after reaction times ranging 15-90 min. It should be highlighted that both catalysts PET/K/urea 1:0.5:0.25 and 1:0.5:0.5 led to higher conversion values, although lower selectivity to quinoline. Experimental results strongly suggest that the nitrogen active sites in catalysts could comprise cyanuric acid or pyridine units at the edges of carbons as almost non-porous samples. DFT calculations for the first step of the reaction would indicate that the low adsorption DH of reagent and product, in the presence of cyanuric acid as reduced model, could be behind of the lower selectivity.

Acknowledgements

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AMB49

(Photo)catalytic transformation of HMF into value-added products

Pedro A. Miranda[1*]**, Ana Cláudia Santos**[2]**, Bruno Valentim**[2]**, Alexandra Guedes** [2]**, Clara Pereira**[1]**,**
Andreia F. Peixoto[1]**, Iwona Kuźniarska-Biernacka** [1]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, Porto 4169-007, Portugal
[2]Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, Porto 4169– 007, Portugal
* *e-mail:up202008689@fc.up.pt*

The use of biomass for production of valuable chemicals, especially catalytic oxidation of 5-hydroxymethylfurfural (HMF) has received extensive attention due to the widespread application of 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) [1]. Photocatalysis using solar energy has emerged as a promising method for selective transformations of HMF under mild and environmentally benign conditions. Various carbonaceous materials (activated carbon, graphene-like materials, carbon nanotubes, etc.) were used to support the semiconductive active sites in order to suppress recombination of photogenerated e^-–h^+ pairs, extend the excitation wavelength, and increase the surface area, *i.e.*, increasing the adsorption capacity of the catalyst. However, silica, an inert material for many reactions, was also used to support semiconductor metal oxides and the combined material exhibited catalytic activity under UV irradiation at room temperature [1].

In this work, the silica rich fraction of coal fly ash (SFA) extracted from bulk coal fly ash was used for preparation of novel hybrid (photo)catalyst for selective HMF oxidation. The resulting hybrid material consists of three components: magnetic $MnFe_2O_4$ (MFO), semiconductor nanoparticles (photoactive centre), silica-rich fraction of industrial ash (support) (SFA) and chitosan (CS) linker. The SFA-CS and SFA-CS-MFO materials were prepared by liquid impregnation based on ionic gelation, using sodium tripolyphosphate as a cross-linking agent [3]. The materials were characterized by various techniques. The significant increase of Fe and Mn amounts from 5.8% and 0.04% (parent sample) to 18.3% and 6.3% (SFA-CS-MFO), respectively, was detected by XRF. Moreover, the presence of characteristic peaks of CS (1640 cm^{-1}, N-H vibration) in the FTIR spectra of SFA-CS and SFA-CS-MFO materials, as well as the diffraction peaks corresponding to the Bragg reflections of MFO in the XRD pattern of SFA-CS-MFO confirmed the successful preparation of the samples.

The as-prepared materials were applied as adsorbents of HMF. The HMF uptake by MFO or SFA-CS-MFO was practically negligible, whereas SFA-CS and SFA showed some HMF adsorption (*ca.* 30% after 24 h contact time). The photocatalytic oxidation of HMF was performed in a quartz glass reactor, illuminated with a 15 W UV-A lamp (Fig. 1) and the composite SFA-CS-MFO showed the best performance (HMF conversion 55% in 360 min) and led to formation of 2,5-furandicarboxylic acid (FDCA) only.

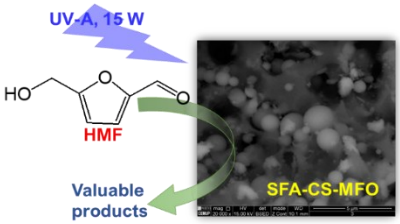

Fig. 1. Photooxidation of HMF

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IKB thanks FCT for funding through program DL 57/2016 – Norma transitória REQUIMTE/EEC2018/14; ACS for PhD scholarship SFRH/BD/131713/2017 and COVID/BD/151941/2021 and AFP for CEEC: 2020.01614.CEECIND/CP1596/CT0007. CP thanks FCT for funding through the Individual Call to Scientific Employment Stimulus (Ref. 2021.04120.CEECIND/CP1662/CT0008).
Pego power plant (Portugal) for the fly ash samples.

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(Photo)catalytic reduction of 4-NPh using TiO_2 from Cork Powder Fly Ashes

Eduardo Mota[1], Renato Guimarães[2], Bruno Valentim[2], Alexandra Guedes[2] Cristina Freire[1], Andreia F. Peixoto[1], Iwona Kuźniarska-Biernacka[1*]

[1]REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[2]Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings,Faculty of Sciences, University of Porto, rua do Campo Alegre s/n, 4169– 007 Porto, Portugal
**iwonakb@fc.up.pt*

The nitroaromatics are toxic and stable compounds extensively utilized in industrial processes, including the manufacture of dyes, pharmaceuticals, pigments, pesticides, wood preservatives, among others. The chemical reduction of 4-nitrophenol (4-NP) to less toxic 4-aminophenol (4-AP) by $NaBH_4$ is of especial relevance in this type of industries [1]. Designing eco-friendly photocatalysts for the photoreduction reactions that generate sustainable sources of energy such as the hydrogen production and in situ transformation of nitro-aromatic contaminants has recently attracted the attention of the scientific community. Among the semiconductor photocatalysts, TiO_2 is the most common photocatalyst especially because its nontoxicity and high catalytic activity and stability. However, TiO_2 is prepared using several costly techniques, including sol-gel, hydrothermal, solvothermal, microwave, and sonochemical methods, which has limited its wide application [2]. In contrast, Cork Powder Fly Ashes (CPFA) are a secondary source of TiO_2 in the form of titanspheres from which it may be recovered [3].

Here for the first time, TiO_2-rich concentrates from CPFA leached with inorganic acid (HCl and/or HF) were used as (photo)catalyst in 4-NP reduction. The TiO_2-rich materials obtained after leaching were characterized via XRF, Raman and SEM-EDS, which confirmed the increasing of TiO_2 concentration upon leaching with the acids. However, the highest TiO_2 concentration resulted from the sequential HCl and HF leaching where the TiO_2 concentration increased from 6 wt.% to 70 wt.%.

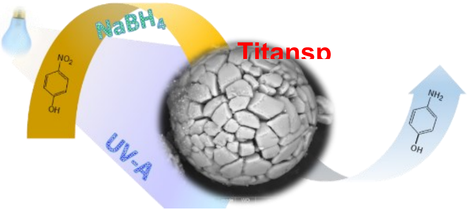

Fig.1. Photocatalytic reduction of 4-NP

The (photo)catalytic reduction of 4-NP (Fig.1) was carried out with TiO_2-rich sample under 60 min irradiation of UV-A light (15 W). The sample with higher TiO_2 concentration showed the highest 4-NP conversion (60 %) whereas the widely used commercial TiO_2 (P25) led to only to 41 % conversion of 4-NP under the same experimental conditions.

Acknowledgments

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Enterprise Relvas II (Mozelos, Portugal) for the fly ash samples.

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High removal of paracetamol by catalytic wet peroxide oxidation with carbon-coated magnetic nanoparticles

Arnaldo V. Dias[1,2*], Adriano S. Silva[2], Ana P. F. da Silva[2], Fernanda F. Roman[2], Jose L. Diaz de Tuesta[2,3], Ysabel Huaccallo[2], Ana M. Lima[1], Helder T. Gomes[2]

[1]Universidade Tecnológica Federal do Paraná, Campus Apucarana, 86812-460 Apucarana, Brazil.
[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal.
[3]Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Spain
ysabel@ipb.pt

The main pollutants in wastewater, such as toxic metals, micropollutants, nutrients, and persistent organic pollutants (POPs) cause negative impacts on the environments and human health. Among these pollutants, the POPs, a group of chemicals that persist in the environment and bioaccumulate through the food web represents a great environmental risk due to their resistance to chemical and biological degradation, and can cause harmful impact on biotic species [1]. The conventional methods to remove POPs, by filtration, flocculation, coagulation and chlorine have not showed promising results, leading to their accumulation in the aquatic environment. However, advanced oxidation processes (AOPs) have emerged as one alternative technology that can degrade organic pollutants. Among the wastewater treatment technologies in this strand, catalytic wet peroxide oxidation (CWPO) has shown potential results in removing a wide range of organic pollutants from wastewater. This technology uses a solid catalyst to decompose H_2O_2 into hydroxyl radicals, the highly oxidizing species promoting pollutant degradation. The solid catalyst typically comprises a metal that acts as the active phase. Nonetheless, carbon materials have also proven to be active in the process due to their electron-transfer capabilities. In this work, magnetic cobalt ferrite nanoparticles (CoFe) were prepared by sol-gel and coated with carbon (CoFeC). Both nanoparticles (bare core and coated nanoparticle) were assessed as catalysts in removing Paracetamol (PCM), chosen as model POPs, by CWPO. Carbon coating involved the formation of a resin made of resorcinol/formaldehyde via the one-pot methodology described in previous works [2]. Oxidation reactions were carried out under 80 °C, pH 3.5, 100 ppm of PCM concentration, and a stoichiometric amount of H_2O_2 to remove the pollutant completely. The results in Figure 1 showed that CoFeC achieved faster H_2O_2 decomposition, leading to a faster PCM removal. Additionally, adsorption tests performed under the same conditions (in the absence of oxidant) showed that pollutant removal by adsorption is insignificant for both materials. These results show one efficient path to upgrade the efficiency of metal-based catalysts in CWPO, with the carbon coating protecting the core from leaching and improving the efficiency of H_2O_2 decomposition.

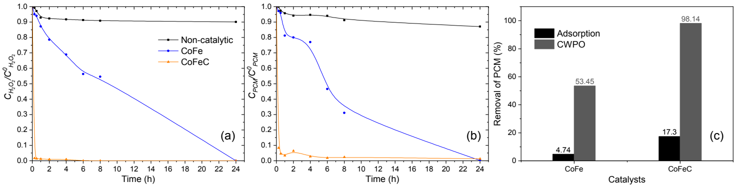

Figure 7. H_2O_2 concentration (a), PCM concentration (b), and comparison between adsorption and oxidation processes (c).

Acknowledgments

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AMB52

A microwave-assisted approach for cellulose extraction from Eucalyptus and Pine tree waste products

Tânia Moniz[1,2,3*], Sílvia Vinhas[1], Mafalda Sarraguça[2], Salette Reis[2] and Maria Rangel[3]

[1] LAQV, REQUIMTE, Dep. Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. do Campo Alegre, s/n, 40169-007 Porto, Portugal
[2] LAQV, REQUIMTE Dep. Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[3] LAQV, REQUIMTE, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
*tmoniz@ff.up.pt

The commonly used procedures for the cellulose extraction from trees waste products are based on non-sustainable chemical and thermal approaches [1, 2]. In this work we describe a new process of cellulose extraction from pine and eucalyptus waste products aiming to develop a simple, efficient, and sustainable approach, microwave-assisted extraction has been considered in all steps of the process.

The methodology includes 3 main steps: i) alkaline treatment; ii) bleaching I, comprising mainly the use of H_2O_2; and iii) bleaching II which consists in an acidic treatment of the wood samples. Figure 1 summarizes all the steps. Samples obtained in each step of the extraction process were characterized by Fourier-transform Infrared (FTIR) spectroscopy, Powder X-ray diffraction (PXRD), thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) and were compared to the starting materials (pre-treated wood) and with the commercially available microcrystalline cellulose. The results point out the applicability of the new approach as a sustainable strategy to obtain cellulose from pine and eucalyptus waste products.

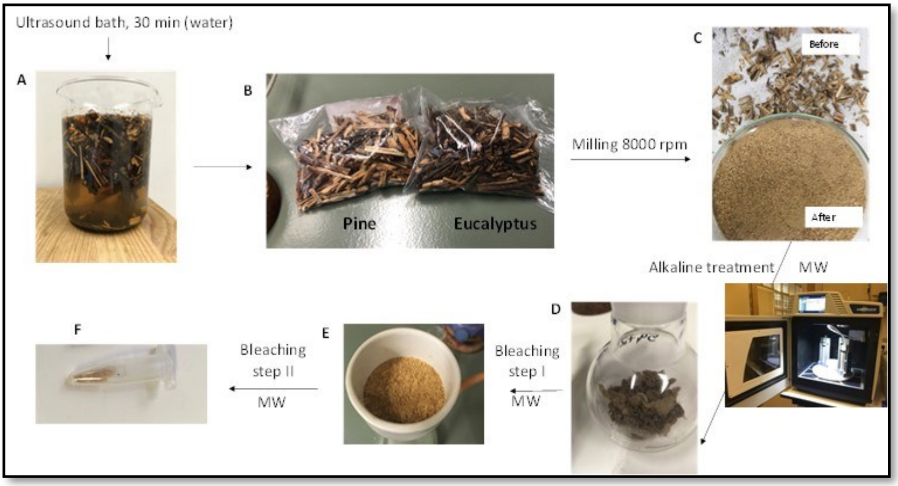

Fig.1. Different steps (A-F) of the developed methodology for cellulose extraction.

Acknowledgements
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Temporal trends of Polycyclic Aromatic Hydrocarbons in soils impacted by a prescribed fire

Maria J. Fernandes[1,2,*], **Manuela Carvalho**[1,] **Felícia Fonseca**[3], **Felipe Macías**[2] **& Cristina Delerue-Matos**[1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, Porto, Portugal;
[2] IIT/LTA- Instituto de Investigaciones Tecnologicas, USC, Santiago de Compostela, Spain
[3]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal
**mea@isep.ipp.pt*

Over the last few years, forest fires have represented one of the major causes of forest devastation, in addition to presenting a risk to life, property, infrastructure and natural resources. The fire effects magnitude on soil properties depends on several factors namely the fire intensity and the post-fire weather conditions. To define strategies, actions, and methods for the soil protection, is essential to understand the process of soil degradation caused by forest fires, their impacts and the context factors that determine them [1].

One of the potential impacts of forest fires on the soil is that they can contribute as a significant source of polycyclic aromatic hydrocarbons (PAHs), not only in the place where the fire occurred but also in the background areas [2], [3]. PAHs, a group of organic compounds with two or more fused aromatic rings mostly formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances present a relatively low solubility in water and are highly lipophilic. Soil contamination by these compounds is of special concern due to their high toxicity, carcinogenicity, environmental persistence, bioaccumulation tendency and diversity of emission sources and levels [3]–[5].

An area exposed to a prescribed fire, located in the Montesinho Natural Park (NE Portugal), was studied. Soil samples were collected at different depths (0-3, 3-6, 6-10 and 10-20 cm), before and after the prescribed fire. The trend of seventeen PAHs concentrations, namely 16 United States Environmental Protection Agency [6] priority congeners and Dibenzo(a,l)pyrene (DB(a,l)P), were monitored up to seven months after the fire. The effects of the prescribed fire were assessed by comparing the PAHs concentration before and after its occurrence. Additionally, some soil characteristics were analysed.

PAHs were analysed using a LC system equipped with photodiode array and fluorescence detectors online. A C18 column was used to the compound's separation, maintained at a room temperature. Each compound was detected at its optimum excitation/emission wavelength pair. External calibrations with PAHs mixed standards in acetonitrile were performed using at least 6 calibration points [7].

Of all the tested compounds, naphthalene (Naph), phenanthrene (Phe), fluoranthene (Fln) and pyrene (Pyr) were the more frequently found in the studied samples. Acenaphthylene (Acen) was the compound found in the highest concentration. Some relationships between the occurrence of fires and the highest concentrations of PAHs were found. In most cases, there was a reduction in the concentration of PAHs with depth as well as with time after the fire.

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Impact of a synthetic aminated 3,4-dioxygenated antifouling xanthone in human retinal cells

Cátia Vilas-Boas[1,2], Logan Running[3], Diana I. S. P. Resende[1,2], Madalena Pinto[1,2], Emilia Sousa[1,2], Marta Correia da Silva[1,2#], Gunes Ekin Atilla-Gokcumen[3*], Diana S. Aga[3*]

[1]FFUP - Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal; [2]CIIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Matosinhos, Portugal; [3]Chemistry Department, University at Buffalo, The State University of New York, Buffalo, NY, USA, 14260.
*ekinatil@buffalo.edu; dianaaga@buffalo.edu

Dedicated by the author to the memory of Professor Costa Lima

Biocide-based coatings are one of the most used and effective strategies to prevent the attachment of marine organisms. However, currently applied biocides, as is the case of the emergent biocide Econea®, are persistent, bioaccumulative, and toxic for target and non-target organisms, including humans [1, 2]. Inspired by natural antifouling (AF) xanthones, a C-1 aminated 3,4-dioxygenated xanthone (compound **1**) was synthesized via reductive amination of 3,4-dimethoxy-9-oxo-9*H*-xanthene-1-carbaldehyde and the appropriate amine and exhibited anti-settlement activity against the larvae of the mussel *Mytilus galloprovincialis* (EC_{50} = 7.28 µM; 3.03 µg/mL) [2]. With proteome studies on mussel plantigrade larvae it was possible to conclude that compound **1** affects myosin isoforms from pedal retractor muscle, responsible for the movement of mussel foot and, consequently, adhesion to surfaces [3]. Lipid metabolism is another important metabolic process that provides energy and supports various physiological and developmental processes. Several AF biocides proved to cause toxicity and oxidative stress to several organisms, triggering alterations in their lipid profile [4].

Due to the lack of toxicity information available on humans for new AF agents, the toxicity of compound **1** using a non-cancerous immortalized retinal pigment epithelial cell line (hTERT-RPE-1) was assessed by a mitochondrial viability assay (MTT) and an IC_{50} value of 77.05 µM was obtained, higher than the commercial biocide Econea® (IC_{50} = 20.29 µM) [3]. Liquid chromatography-quadrupole time of flight mass spectrometry (LC-Q-TOF/MS) was used to assess the impact of compound **1** (10 µM) on the cellular lipidome [4]. Compound **1** causes depletion in 43 lipids, especially in ceramides C18:0, C18:1, C22:1, diacylglycerol C38:5, dihydroceramide C16:0, deoxyceramide C22:1, dihydro-sphingomyelins C14:0, C16:0, phospholipids C44:5, C44:6, sphingolipid C26:1, and triacylglycerols C56:8, C58:8 (<0.5-fold change). The opposite trend was observed after Econea® exposure, which causes accumulation on several lipids involved in cell death, membrane modeling, lipid storage, and oxidative stress [4].

These results in human retinal lipidome, added to the previous proteomic studies on mussel larvae, indicate minimal impact of compound **1** on both marine and human health.

Acknowledgments
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Mejora de la capacidad de adsorción de *hydrochar* de alperujo en la eliminación de compuestos farmacéuticos mediante la funcionalización en un solo paso con grupos amino

Silvia Escudero-Curiel[1, *], **Marta Pazos**[1], **Ángeles Sanromán**[1]

[1]CINTECX. Universidade de Vigo, Departamento de Ingeniería Química. Campus As Lagoas-Marcosende, 36310
Vigo, España
**sescudero@uvigo.gal*

En la última década, la preocupación por la escasez de agua ha ido en aumento debido principalmente al cambio climático con el telón de fondo de la contaminación acuática mundial. Por tanto, es esencial aplicar medidas de remediación para garantizar el acceso al agua potable en los próximos años. Dentro de los contaminantes, sobre los que se centran los esfuerzos para controlar su presencia en todo tipo de masas de agua, se encuentran los compuestos farmacéuticos, debido a su potencial para causar efectos adversos en los organismos acuáticos y en la salud humana [1]. En este sentido, los procesos de adsorción han demostrado ser muy eficaces y de sencilla aplicación industrial, permitiendo la concentración y rápida separación de los contaminantes del medio líquido. La búsqueda de nuevos materiales adsorbentes eficientes, rentables y respetuosos con el medio ambiente es quizás el punto más crítico de esta técnica. En aras de generar productos de valor añadido, el empleo de residuos agroindustriales como material de partida para producir materiales carbonosos con fines de adsorción es, sin duda, una de las mejores alternativas en estudio. La capacidad de adsorción de estos materiales carbonosos está muy influenciada por la materia prima y las condiciones de carbonización aplicadas (temperatura, relación sólido/líquido y tiempo de residencia) [2]. La carbonización hidrotermal (HTC por sus siglas en inglés) o pirolisis húmeda se emplea en residuos con un contenido en agua mayor al 50% como es el caso del alperujo obtenido de la extracción del aceite de oliva, residuo mayoritario producido por esta importante industria. El objetivo de este estudio fue valorizar un residuo abundante como el alperujo mediante la optimización de un proceso de HTC para obtener un buen material adsorbente. Se evaluó el efecto de la temperatura (160-220 ºC), el contenido de sólidos (25-50%) y el tiempo de residencia (1.5-2.5 h) sobre la capacidad de adsorción de los *hydrochar* sintetizados. Para ello se usaron dos fármacos, fluoxetina (FLX) y cefazolin (CFZ), los cuales, en el rango de pH del estudio (4-9), tienen una carga neta positiva y negativa, respectivamente. Aunque se obtuvieron porcentajes de eliminación de hasta el 80% para FLX, sólo se obtuvo un 7% para el CFZ. Este hecho probablemente es debido a que, al pH de trabajo, la superficie del *hydrochar* está cargada negativamente (por encima de su punto de carga cero) y la del FLX es positiva, pero la del CFZ es negativa, lo que produce una repulsión electrostática. El gran contenido en grupos funcionales del *hydrochar* de alperujo ofrece una superficie adaptable sobre la que se pueden realizar diferentes funcionalizaciones para mejorar su eficiencia de adsorción. Así, para mejorar los rendimientos de adsorción, se planteó una funcionalización con grupos amino que podrían ayudar a aumentar las cargas positivas en la superficie. Las funcionalizaciones se llevaron a cabo en un solo paso, es decir al mismo tiempo que se producía el *hydrochar* y para ello se utilizaron dos compuestos diferentes, urea y polietilenimina (PEI). La funcionalización en un solo paso con PEI ofreció buenos resultados, con una eliminación del 93% y el 61% para CFZ y FLX respectivamente. Estos resultados son prometedores y demuestran que la funcionalización en un solo paso con grupos amino abre una vía para modificar los *hydrochars* y utilizarlos como adsorbentes versátiles que cubren una amplia gama de compuestos.

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Efecto del envejecimiento marino natural *vs* simulado en el contenido metálico de microplásticos de biopolímeros

A. Carlosena-Zubieta[*], **J. Terán-Baamonde, R.M. Soto-Ferreiro, E. Alonso-Rodríguez y S. Muniategui-Lorenzo**

Universidade da Coruña, Grupo de Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Departamento de Química. Facultad de Ciencias, Campus de A Coruña s/n, 15008, A Coruña
**alatzne.carlosena@udc.es*

El uso de biopolímeros y materiales reciclados es uno de los principales pilares aplicados en términos de economía circular, a partir del cual la UE está intentando poner freno a la problemática del imparable crecimiento de los residuos plásticos generados [1]. Sin embargo, y al igual que para el caso de los polímeros convencionales, la utilización de estos plásticos alternativos no está exenta de potenciales riesgos desde un punto de vista medioambiental o sobre la salud humana.

Para llevar a cabo la evaluación de dichos riesgos es importante realizar un estudio sobre el comportamiento de los compuestos o especies químicas presentes en el propio plástico o con los que entre en contacto este material. En este trabajo, microplásticos (MPs) de tres biopolímeros (ácido poliláctico-PLA, polihidroxibutirato-PHB y polihidroxibutirato-hidroxivalerato-PHBv) se sometieron a un proceso de envejecimiento en medio marino, tanto de forma natural como simulada en laboratorio, con el fin de determinar su efecto en la composición metálica de estos materiales. Para ello, los MPs de cada biopolímero se mantuvieron sumergidos durante 90 días en el mar (zona portuaria) y en probetas con agua de mar en el laboratorio, bajo condiciones de irradiación solar, penetración de la luz, agitación, estrés mecánico y temperatura similares a las que existirían en el medio natural [2]. Una vez finalizado el periodo de envejecimiento, se determinó el contenido metálico en los MPs mediante ICP-MS, previa digestión ácida asistida por microondas. También se analizaron las muestras inicialmente para determinar su contenido metálico intrínseco.

Los resultados muestran que el PHB y PHBv contienen Cr, Cu, Fe, Hg, Ni, Pb y Sn mientras que el PLA presenta Fe, Hg y Sn, destacando su alto contenido en Sn (25 mg/kg^{-1}). En el proceso de envejecimiento, tanto natural como simulado, se observó una disminución del contenido de la mayoría de los metales, siendo liberados en el medio natural en mayor medida. Mientras que algunos elementos incrementaron su concentración, como el Fe y Mn en el medio natural y Cd y Cr en el medio simulado.

A la vista de los resultados y comportamiento en términos de contenidos metálicos a lo largo del tiempo, se puede concluir que los resultados alcanzados en el ensayo de envejecimiento marino simulados en el laboratorio pueden verse influenciados por ciertos aspectos que no son totalmente equivalentes a las condiciones naturales, teniendo que tratar estos datos con precaución y siendo necesarios estudios en mayor profundidad. Por otra parte, se confirma que los MPs de biopolímeros también constituyen un riesgo potencial comportándose como vectores de contaminación metálica en el medio marino.

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Cork by-products extracts with added-value for the cosmetic industry

Claúdia Pinto[1], Sara Cravo[1,2], Ana Silva[3], Sandra Mota[4,5], Joana Rocha e Silva[6], Carlos Afonso[1,2], Maria Elizabeth Tiritan[1,2,7], Maria Teresa Cruz[3,4], Honorina Cidade[1,2,*], Isabel F. Almeida[4,5]

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2]CIIMAR–Interdisciplinary Centre of Marine and Environmental Research, University of Porto, 4450-208 Matosinhos, Portugal
[3]Center for Neuroscience and Cell Biology, 3004-504 Coimbra, Portugal
[4]UCIBIO – Applied Molecular Biosciences Unit, MedTech, Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[5]Associate Laboratory i4HB - Institute for Health and Bioeconomy, Faculty of Pharmacy / Faculty of Medicine, University of Porto, 4050-313 Porto, Portugal
[6]Dimas & Silva, Lda. Industry, Rua Central de Goda 345, Mozelos, Portugal
[7]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, CESPU, CRL, 4585-116 Gandra, Portugal
[3]Faculty of Pharmacy, University of Coimbra, 3000-548 Coimbra, Portugal
**hcidade@ff.up.pt;* dedicado pela autora à memória do professor Costa Lima

The development of sustainable products is an important issue over recent years. The cosmetic industry is not an exception, and the upcycling of by-products from agro-industrial waste is increasingly explored. Cork, the outer bark of *Quercus suber* L., finds use in diverse applications, namely for the wine and building industries. As a result, cork residues are produced, such as the cork powder, without commercial interest, which, therefore, is rejected and burned for energy production, despite containing valuable bioactive compounds [1]. Herein, extracts of cork powder were prepared by solid/liquid extraction, using ecofriendly extracting solvents of recognized harmlessness and skin compatibility. The number of extractions, extraction time and temperature were optimized in order to obtain extracts with high antioxidant activity. The antioxidant activity of all extracts was screened by the DPPH assay according to previous work [2]. For the extracts showing higher DPPH scavenging activity, total phenolic content and cytotoxic profile in keratinocytes (HaCaT) were determined, visioning a potential skin application. Overall the results showed that extracts with strong antioxidant potential and low cytotoxic effect can be obtained from the processing of waste streams, promoting a sustainable and circular bioeconomy.

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Hexachlorocyclohexane adsorption assays on two moss species for biomonitoring purpose

Chaos, Z.[1*], Pérez Alonso, P.[1], Fernández, J. A.[2], Aboal, J. R.[2], Monterroso, C.[1]

[1]CRETUS, Dept. Edafoloxía e Química Agrícola, Universidade de Santiago de Compostela,
15782 – Santiago de Compostela, Spain

[2]CRETUS, Dept. Bioloxía Funcional, Universidade de Santiago de Compostela,
15782 – Santiago de Compostela, Spain
**mzoe.chaos@usc.es*

Mosses can retain pollutants and be used as biomonitors due to their high tolerance to contamination, their easy handling and their availability [1]. However, there is no evidence of its potential to retain hexachlorocyclohexane (HCH), a persistent organochlorine pollutant of global concern [2].

In this study, adsorption of α-, β-, γ- and δ-HCH on two mosses cultivated *in vitro* and devitalized (*Fontinalis antipyretica* Hedw. and *Sphagnum palustre L.*) was evaluated through a batch experiment of successive additions of a contaminated aqueous solution. After 24 h under agitation, the equilibrium concentration (C_E) was determined by ultrasound-assisted extraction with hexane (1:1, v/v) and the followed analysis by GC/MS (gas chromatography - Model 450 GC, Agilent Technologies - coupled to a mass spectrometer - Model 220 MS, Agilent Technologies -). Phenanthrene-d10 was used as internal standard. The method was validated with recoveries over 95 % and quantification limits between 0.9 and 5 ng L^{-1} depending on the isomer. Retention capacity was calculated by the difference of the C_E with the added concentration of HCH and sorption models (Langmuir, Freundlich and Linear equation) were used for quantitative description of sorption processes.

In general, both the adsorption kinetics and the adsorption capacity showed significant differences between the two mosses, being the *F. antipyretica* the one that showed the higher affinity for HCH. The maximum retention of HCH in *F. antipyretica* was 4792 mg of the sum of HCH isomers per kg of moss, adjusting to the Freundlich and Linear models. While the retention in *S. palustre* was minimal and did not adjust the tested models. The physico-chemical characterization of the mosses together with the results of other studies [3] indicate that the composition of the cell walls could be related to the different adsorption capacity of the mosses. In vitro-produced clones of *F. antipyretica* can be considered as potentially adequate for environmental monitoring of HCH, although further research is needed.

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Application of Advanced Oxidation Processes to Industrial and Agro-industrial Wastewater for Energy Production: a Review

Ana Gomes[*], **Amadeu Borges, José A. Peres, Marco S. Lucas**

Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5000-801 Vila Real, Portugal
* *apgomes@utad.pt*

The rapid world population growth allied to the industrial and economic development of modern societies enhances energy consumption and waste generation [1]. Industrial and agro-industrial wastewaters are a major environmental problem that need to be properly addressed. Wastewater treatment requires a large amount of energy, being an obstacle to its realization in the developing world; thus, the ability to harvest energy directly from wastewater would be reframing [1, 2].

The use of wastewater for bioenergy production can be carried out, however, some pre-treatments can be required, due to its recalcitrant composition [3]. Different pre-treatment methods can be employed such as traditional methods that include chemical treatment, physical treatment and biological treatment [4]. However, the high costs and energy consumption and their low effectiveness in degrading persistent compounds lead to the need of pursuing alternative technologies [1].

Advanced Oxidation Processes (AOPs) can be a suitable alternative to pre-treat the wastewater biomass and degrade the recalcitrant compounds. These processes involve the generation of highly reactive radicals, especially hydroxyl radicals ($HO^•$), that are powerful in oxidizing recalcitrant and toxic compounds which can result in their mineralization or increase of biodegradability. These reactive radicals attack the organic molecules rapidly and non-selectively [5]. Some of the AOPs have been used as wastewater pre-treatment for further bioenergy production, such as ozonation, Fenton reagent, hydrogen peroxide [1], ultraviolet radiation, photocatalysis [6], ultrasound [2], wet air oxidation [7], microwave radiation [8] and electrochemical oxidation [9]. Therefore, AOPs seem to be promising technologies in the pre-treatment of recalcitrant substrates for bioenergy production.

This work intends to provide a state-of-the-art of the application of AOPs to industrial and agro-industrial wastewaters to enhance bioenergy production.

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A novel, green and fast chromatographic method to quantify nystatin in pharmaceutical samples: development and validation

Filipa Sousa[1,*], **Domingos Ferreira**[1,2], **Salette Reis**[3], **Paulo Costa**[1,2]

[1] UCIBIO – Applied Molecular Biosciences Unit, MedTech-Laboratory of Pharmaceutical Technology, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2] Associate Laboratory i4HB - Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[3] LAQV-REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal
**fsousa@ff.up.pt*

Nystatin is a polyene antifungal drug with fungicidal activity against several pathogens. Its unstable chemical nature and very low dissolution in physiological fluids complicate its analysis and quantification and, therefore, limits its application in therapeutics [1].

In this study a novel High Performance Liquid Chromatography method for the assay of nystatin was developed and validated. The method was performed on a reverse phase-C18 column and a flow rate of 1.0 mL/min. According to ICH guidelines it became evident that the method was linear over the range of 0.250–15.000 µg/mL, with regression equation: $y = 0.214x + 0.119$, by least squares method, delivering good determination coefficient ($r = 0.9958$). The method's detection and quantification limits were 1.396 and 4.231 µg/mL. This method was sensitive and selective, presenting several advantages over the ones described in the Portuguese Pharmacopoeia and in similar literature reports (Table 1).

Table 1. Comparison of several chromatographic parameters described to quantify nystatin in the Portuguese Pharmacopoeia [2], similar literature reports [3-5] and in this method.

Chromatographic Parameter	Portuguese Pharmacopoeia	Similar literature reports	New method
Column dimensions	150 mm x 4.6 [2]	250 mm x 4.6 [3,4] 150 mm x 4.6 [5];	100 mm x 4.6
Mobile phase	Acetonitrile : amonium acetate solution 3.85 g/L (29:71 or 60:40 v/v) [2]	Ammonium acetate 0.05 M buffer : methanol (30:70) [3,4]; 1% acetic glacial acid, acetonitrile : water (40:60, v/v) [5];	Methanol : water acidified to pH3 with acetic glacial acid (75:25 v/v)
Solvents to solubilize/dilute nystatin	Dimethyl formamide and buffer solution pH6 [2]	Ammonium acetate 0.05 M buffer : methanol (30:70 v/v) [3,4]; Stock solution in dimethyl sulfoxide and standard solutions in methanol : dimethyl formamide : water (55:15:30, v/v/v) [5];	Phosphate-citrate buffer solution pH5.5
Injection volume	20 µL [2]	20 µL [3,4]; 50 µL [5]	10 µL
Total run time	>15 min [2]	5 min [3]; >16 min [4]; 8 min [5]	5 min

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Excess sludge treatment by dewatering and consecutive adsorbent production

Udaondo Ana[1], **Montes Vicente**[1], **Gimeno Olga**[1], **Rivas F. Javier**[1], **Beltrán Fernando. J**[1]

[1]Instituto Universitario de Investigación del agua, Cambio Climático y Sostenibilidad (IACYS), Av. de la Investigación s/n, Badajoz, España
**anaudaondo@unex.es*

El tratamiento de las aguas residuales está en continuo desarrollo en la mayoría de los países, siendo un reto la lucha contra la escasez de agua del planeta y, por consiguiente, la gestión de los lodos generados en el tratamiento. La gestión de lodos de depuradora es uno de los problemas ambientales más complejos asociados al tratamiento de aguas residuales. La adecuada gestión y la eliminación del exceso de lodos que se generan en las estaciones depuradoras de aguas residuales urbanas, se va a convertir en uno de los objetivos más importantes desde el punto de vista económico y de protección del medio ambiente en la próxima década. El vertido de los mismos y su gestión inadecuada, provocan múltiples impactos ambientales, como: problemas de salud pública, emisiones de gases de efecto invernadero y contaminación por nitrógeno. Por todo lo anterior, debe gestionarse adecuadamente, ya sea para su eliminación o reutilización. Los destinos del mismo hoy día son: biogás, aditivo para fertilizantes y vertedero.

Por ello, en el presente trabajo, se propone un método alternativo para su reutilización, en el cual, primeramente, los lodos son sometidos a un tratamiento de deshidratación que facilita su procesamiento posterior al ahorrar costes y energía en su gestión [1]. La deshidratación consistió en tratar el residuo con temperatura y peróxido de hidrógeno. De esta manera, se mejoró notablemente la sedimentación y separación del agua de los lodos. Posteriormente, el lodo deshidratado, se valorizó produciendo carbón activo por distintas vías. Por un lado, se hicieron carbones por activación física con N_2 a 400 y 700ºC (S_{400} y S_{700} respectivamente). Por otro, se activaron los carbones químicamente empleando KOH (S_{KOH}), siendo este último, el método más descrito en bibliografía. No obstante, dicha activación con hidróxido de potasio genera un residuo químico adicional. Como novedad, se empleó el químico NH_4NO_3 (S_{NN}) como activante, el cual se descompone en N_2 y H_2O inocuos para el medioambiente.

En la Tabla 1 se muestran los principales resultados de los carbones obtenidos, observándose que el que proporciona mayor rendimiento (S_{400}) conduce a un área superficial (BET) menor, mientras que los activados con mayor Tª, con o sin químico, tienen un rendimiento por debajo de 60%. No existe una relación directa entre el área superficial y la adsorción de Fenol, siendo S_{NN}, la principal novedad, el mejor adsorbente.

***Tabla 1**. Principales características de los carbones obtenidos.*

Carbón Activo	*Tª de activación física (ºC)*	*Activante químico y Tª (ºC)*	*Rendimiento (%)*	*BET (m2/g)*	*Capacidad de adsorcion de Fenol (mg/g)*
S_{400}	400	None	78.20	96.41	3.53
S_{700}	700	None	59.45	185.06	3.70
S_{KOH}	None	KOH/800	56.66	142.80	2.59
S_{NN}	None	NH_4NO_3/400	49.44	117.43	4.97

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Novel Pitavastatin Calcium Forms: Insights Into a Complex Solid State System

João A. V. Santos[2], Francesca Peluso[3], M. C. Gamberini[3], Giusi Piccirillo[2], João A. Baptista[2], Teresa M. R. Maria[2], João Canotilho[1,2,*], Ricardo A. E. Castro[1,2], M. Ermelinda S. Eusébio[2]

[1]Faculdade de Farmácia, Universidade de Coimbra, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
[2]CQC/IMS, Centro de Química de Coimbra/Institute of Molecular Sciences, Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal
[3]Department of Life Sciences, University of Modena and Reggio Emilia, via Campi n.183, 41125 Modena, Italy
**jcano@ff.uc.pt*

Drug development has been a growing area of interest for the scientific community, with research on active pharmaceutical ingredients (APIs) being highly regarded as a pivotal field for society in the modern world. In turn, APIs bioavailability and solid-state behavior are key challenges when dealing with drug development, prompting studies regarding polymorphism, solvates, amorphous phases and other solid forms.[1]-[3]

Pitavastatin calcium (PIT) stands as a high impact statin, being recognized for its pleotropic effects, which provides well-known pharmaceutical benefits. However, beyond a few patents where some information can be found, there is a major lack of information concerning this statin solid state.[4]-[6]

Hence a thorough characterization of commercial drug sample was carried out, followed by polymorph screening using mechanochemical and crystallization from solution techniques. PIT samples were characterized by Attenuated Total Reflectance-Fourrier Transform Infrared (ATR-FTIR) spectroscopy, Differential Scanning Calorimetry (DSC), X-ray Powder Diffraction (XRPD), Thermogravimetric Analysis (TGA), and Polarized Light Thermomicroscopy (PLTM).

The results led to important findings concerning the initial state of PIT. In addition, several solvents with baffling behavior were identified, including a family of isostructural forms comprising different solvent compositions in a similar crystalline structure.

These discoveries clearly exposed the complexity of pitavastatin calcium solid state, unraveling the versatility of this statin in what concerns the formation of new solid forms and paving the way for future applications of this puzzling API for pharmaceutical use.

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Bromothymol Blue and Bromocresol Green removal using chitin as a sorbent material: pH, kinetic and equilibrium studies

D. Vázquez[*], J.L. Barriada, R. Herrero.

Centro de Investigaciones Científicas Avanzadas (CICA), Rúa As Carballeiras, 15008 A Coruña, España.
Departamento de Química, Universidade da Coruña (UDC), Rúa da Fraga 10, 15008 A Coruña, España.
**david.vazquezg1@udc.es*

El agua es, sin duda, el recurso natural más importante para la vida humana y fundamental para su desarrollo. Sin embargo, en los últimos años se ha producido un gran deterioro de los acuíferos debido al elevado número de vertidos que terminan contaminando este recurso natural [1]. De hecho, en 2021, el porcentaje de efluentes acuosos contaminados emitidos al medio ambiente que no recibieron ningún tratamiento previó alcanzó más del 80 % a nivel global, por lo que la eliminación de contaminantes en medio acuoso continúa siendo un problema de gran importancia hoy en día [2].

En la actualidad, se producen diariamente $7 \cdot 10^7$ toneladas de colorantes orgánicos en todo el mundo para su uso en industrias textiles [3]. En cambio, cerca de un 10 % de esta producción desemboca en los medios acuáticos, dañando a los organismos que allí habitan y consecuentemente a la salud humana por sus propiedades cancerígenas y mutagénicas [3]. Para disminuir tanto los porcentajes de contaminación acuática como de emisión de colorantes, es necesario investigar la aplicación técnicas eficaces y de bajo coste que den solución a esta problemática.

En este trabajo se estudia la eliminación de dos colorantes orgánicos, azul de bromotimol y verde de bromocresol mediante técnicas de adsorción por ser esta una alternativa eficaz, sostenible y de bajo coste, lo que favorece su aplicabilidad frente a otros procesos como son la evaporación, precipitación, electrolisis, intercambio iónico etc [3]. Como material adsorbente se empleará la quitina, un polímero natural directamente extraído del exoesqueleto de crustáceos marinos *(Maja sp.)*. Para llevar a cabo una correcta eliminación se han estudiado varios parámetros con el objetivo de optimizar las condiciones de adsorción siendo de particular importancia la influencia del pH, así como un estudio tanto de la cinética del proceso como de su equilibrio, construyendo finalmente isotermas de adsorción.

Los resultados muestran que el máximo de adsorción se obtiene a pH = 4 para ambos colorantes. El tiempo que se tarda en alcanzar el equilibrio es de 90 min para el azul de bromotimol y 80 min para el verde de bromocresol, siendo el modelo cinético de pseudo-segundo orden el que mejor ajusta los datos experimentales. Finalmente, el modelo de Langmuir permite describir adecuadamente el equilibrio de adsorción con valores de capacidad máxima de adsorción (Q_{max}) elevados de 106 $mg \cdot L^{-1}$ para el azul de bromotimol y de 113 $mg \cdot L^{-1}$ para el verde de bromocresol.

En conclusión, estos resultados demuestran que la quitina puede emplearse en columnas fijas para el tratamiento de efluentes o aguas contaminadas por estos colorantes.

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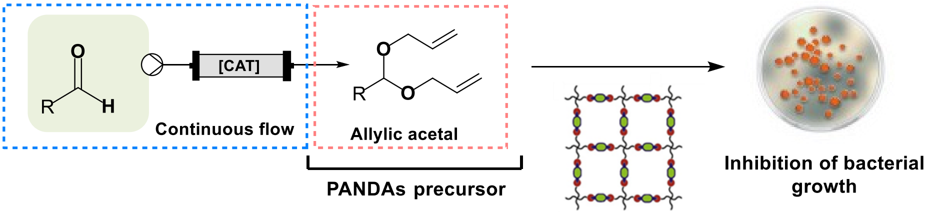
Development of Potential Antibacterial Agents through Sustainable Synthetic Strategies

Madalena F. C. Silva[1,*], **Rafael T. Aroso**[1], **Gabriela J. da Silva**[2], **Fábio M. S. Rodrigues**[1], **Rui M. B. Carrilho**[1] **and Mariette M. Pereira**[1],

[1]CQC, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal [2]FFUC, Faculty of Pharmacy, University of Coimbra, Health Sciences Center, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
**madalenacunhasilva@gmail.com*

The increasing emergence of multidrug-resistant bacteria has led to a growing need to develop new chemical entities and/or alternative therapies. [1] Within the scope of the development of new chemical entities, molecules with the allylic acetal function can be incorporated in pro-antimicrobial networks via degradable acetals (PANDAs) for the sustained release of an antibacterial agent with the aldehyde function, which constitute a research area of high scientific interest. [2, 3, 4]

In this work, we present the preparation of allylic acetals as potential precursors of PANDAs, using reusable heterogeneous acid catalysts. Due to the interest regarding the implementation of safer operation conditions and sustainability, the acetalization reactions were first conducted in batch systems and then transposed and optimized in continuous flow systems (scheme 1). This technology clearly demonstrated higher efficiency, achieving high conversion (97%) with low residence times (10 min). Furthermore, the antibacterial activity of the aldehydes that could be integrated in PANDAs, and released as antibacterial agents upon the acetal hydrolysis, was evaluated. Among the aldehydes tested against *E. coli* ATCC 25922, 3-phenylpropanal achieved the highest antibacterial activity, with an inhibition diameter value of up to 14 mm.



Scheme 1. Continuos-flow synthesis of allylic acetals as potential precursors of PANDAs.

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Highly efficient transition metal-doped carbon catalysts for the selective synthesis of quinoxalines

Elena Pérez-Mayoral[1]*, Marina Godino-Ojer[2]*, Sergio Morales-Torres[3], Francisco J. Maldonado-Hódar[3]*

[1] Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Facultad de Ciencias, Urbanización Monte Rozas, Avda. Esparta s/n Ctra. de Las Rozas al Escorial Km 5, 528232 Las Rozas, Madrid, Spain
[2] Facultad de Ciencias Experimentales, Universidad Francisco de Vitoria, UFV, Ctra. Pozuelo-Majadahonda km 1.800, 28223 Pozuelo de Alarcón, Madrid, Spain
[3] NanoTech-Nanomaterials and Sustainable Chemical Technologies. Faculty of Sciences. University of Granada. Avda. Fuente Nueva s/n, 18071, Granada. Spain
*eperez@ccia.uned.es

Nanostructured carbon gels are materials of great interest with application in catalysis. Considering the high potential of carbon aerogels for the synthesis of heterocyclic systems [1, 2], and that transition metals (TM) have been extensively investigated for quinoxaline catalytic synthesis, especially the first-row ones due to the greater abundance, low toxicity, low cost, among other advantages, we report herein different carbon aerogels doped with different TM - Mo, Fe, Co and Cu -, prepared from different metal precursors although maintaining the synthesis conditions, active and selective in the synthesis of quinoxalines. Quinoxalines are nitrogen-containing heterocycles as part of biologically heterocyclic scaffolds of great pharmacological interest.

Carbon aerogels doped with TM were prepared according to methods revised by Pastrana-Martínez et al [3]. These materials present differences on porosity and oxidation states of metallic phases depending on the used metal precursor and carbonization temperature. Investigated carbon aerogels are macroporous samples showing S_{BET} ranging to 286-660 m^2/g, Co-500 as an exception (mesoporous sample). The metal phase in Fe and Mo-doped carbons is mainly as the oxide form, whereas in Co or Cu-doped aerogels consisting of Co^0 or Cu^0 nanoparticles.

TM-doped carbon aerogels were tested in the synthesis of quinoxalines from *o*-phenylenediamine and benzoin, at 100 ºC, using toluene as solvent, activity varying as follows: Mo ~ Co > Fe > Cu. Remarkably, Mo and Cu aerogels were found to be the most and the least active catalysts, respectively, both selectively yielding the corresponding quinoxaline as the only reaction product. It is noteworthy that reaction rate decreases with the time in the presence of Fe and Co aerogels and the formation of hydrogenated intermediate species, which suggests a lower dehydrogenation capacity of these materials. These results indicate that operative reaction route probably consists of i) imination reaction, ii) imine-enamine tautomerization, iii) heterocyclization, iv) dehydration and, finally, v) dehydrogenation, in accordance with previous results recently described by us. In all the cases, the high porosity of the aerogels facilitates a good diffusion of the reagents and reaction products.

Acknowledgements

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AMB66

Silica-supported molybdenum oxide catalysts for efficient and selective synthesis of quinoxalines

Elena Pérez-Mayoral[1]*, Marina Godino-Ojer[2]*, Rodrigo Blázquez García[1], Carlos A. Ortiz-Bravo [3]*

[1] Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Facultad de Ciencias, Urbanización Monte Rozas, Avda. Esparta s/n Ctra. de Las Rozas al Escorial Km 5, 528232 Las Rozas, Madrid, Spain.
[2] Facultad de Ciencias Experimentales, Universidad Francisco de Vitoria, UFV, Ctra. Pozuelo-Majadahonda km 1.800, 28223 Pozuelo de Alarcón, Madrid, Spain.
[3] Departamento de Físico-Química, Instituto de Química, Universidade Federal Fluminense, Outeiro de São João Batista, Campus do Valonguinho, Niterói, Rio de Janeiro, Brazil.
eperez@ccia.uned.es

Silica-supported molybdenum oxide catalysts have been extensively used for important reactions, such as olefin metathesis and selective oxidation of alcohols, alkanes, and alkenes [1]. However, the use of these catalysts is not widespread for the synthesis of heterocyclic compounds with biological activity.

In this communication, we used a series of silica-supported molybdenum oxide catalysts with Mo loadings of 0.5, 1.0, and 3.0 wt.% (*i.e.*, SiMo0.5, SiMo1, and SiMo3) for the synthesis of quinoxalines, from *o*-phenylenediamine and α-hydroxyacetophenone, as an important heterocyclic motif in a plethora of natural products, agrochemicals and synthetic compounds showing a wide variety of biomedical applications. The XRD patterns of the materials show diffraction peaks associated with the crystalline hexagonal MoO_3 phase only for SiMo3, indicating that Mo oxides are as either completely dispersed or amorphous phases at lower loadings. The specific surface area of the samples slightly decreased with Mo loadings. On the other hand, FTIR spectra show that the intensity of the band at 3745 cm^{-1}, related to hydroxyls on external Si sites (Si-OH) [2], decreases progressively with increasing Mo loadings, suggesting Mo preferentially anchors at Si sites.

Regarding the catalytic activity, all the catalysts were efficient in the synthesis of quinoxalines. The SiMo3 catalyst, with the highest Mo loading, was the most efficient, selectively leading to the corresponding quinoxaline with 95% of conversion, after 180 min of reaction. Highly dispersed catalysts, SiMo1 and SiMo0.5, presented similar conversions and high selectivity. In summary, we report herein a new family of silica-supported molybdenum oxide catalysts, easily prepared, highly efficient, and selective for the quinoxaline synthesis under mild reaction conditions.

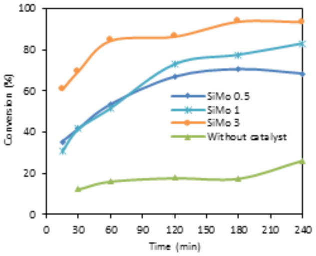

Fig.1. Conversion *vs*. time for the synthesis of quinoxalines, at 353 K, catalyzed by silica-supported molybdenum oxide catalysts.

Acknowledgments
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AMB67

Adsorption of volatile fatty acids with activated carbons produced from olive pomace

Ana Paula Ferreira da Silva[1,2*], Jose L. Diaz de Tuesta [1,2], Teresa Alvarino[3], Anton Taboada-Santos[3], Helder T. Gomes [1,2].

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[3] Fundación Centro Gallego de Investigaciones del agua (CETAQUA), Vila da Auga, Rúa José Villar Granjel, 15890, Santiago de Compostela, España

**anapaula.silva@ipb.pt*

Recently, volatile fatty acids (VFAs) attracted much attention due to their low-cost production from different types of wastes through dark fermentation, potentially leading to the sustainable production of fuels, materials or chemicals while diminishing the waste volume. However, the recovery of these materials is still a challenge. An adsorption process was applied on model waters containing VFAs (butyric - BA, propanoic - PA and acetic acid - AA) to adsorb and recover them using two different types of activated carbons [1,2]. The activated carbons used in this study were materials valued from the biomass of olive pomace: activated carbon (AC) and biochar (BI).

The adsorption was carried out at 50 ºC with constant agitation for 2 h, and the adsorption of the VFAs was monitored by taking samples at 15, 30, 60 and 120 min. The initial concentration of VFAs was 2.5 g/L each and 2.5 g/L of adsorbent. The initial pH of each solution was measured, being 2.35 for AA, 2.43 for AP and 2.52 for AB. The adsorption results with CA and BI can be seen in Figure 8 below.

The adsorbent AC was able to adsorb 40% of AA, 36% of AP and 48% of AB at the end of 120 min, while for BI the removal was 12% of AA, 56% of AP and 64% of AB. It is possible to analyze that the AC had a similar performance for all AGVs; however, the adsorbent BI had a better performance to adsorb AP and AB with adsorption rates greater than 50%; nonetheless, the adsorption of AA was insufficient. The final pH was also measured after 120 min of the experiment, being 2.7 for AA, 3.23 for PA and 3.08 for BA (the same initial pH and final pH results were obtained in the adsorption experiment with BI).

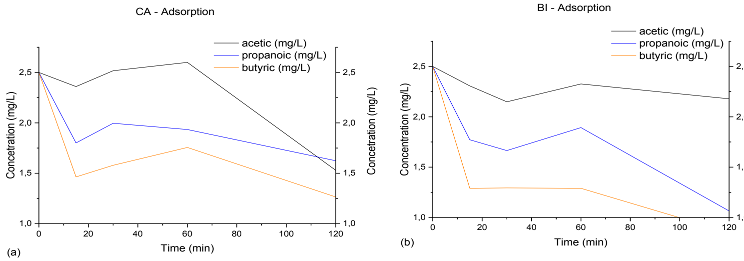

Figure 8: VFA concentration profile upon experiment time (a) activated carbon and (c) biochar.

Acknowledgments

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AMB68

Production and Characterization of Geopolymeric Mortars From Diatomaceous Earth

Júlia F. Murta[1,2,3]*, Ana Paula Ferreira da Silva[1,2]*, Leandro Magalhães[1], Debora Macanjo[1,4], Carlos Eduardo dos Santos.[3], Helder T. Gomes [1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3] Departamento de Engenharia de Materiais, Centro Federal de Educação Tecnológica de Minas Gerais, 30421-169 Belo Horizonte, Brasil
[4] C-MADE Centro de Materiais e Tecnologia Construtivas, Universidade Beira Interior (UBI).
**anapaula.silva@ipb.pt*

Due to the high release of carbon dioxide into the atmosphere, the earth's average surface temperature has increased. Heat waves, melting of glaciers and animal deaths are some visible consequences. Deforestation, agriculture, transportation and industries are major contributors to CO_2 emissions [2]. For instance, Portland Cement generates high pollution levels, responsible for around 7% of global carbon dioxide emissions [3]. For this reason, Portland cement alternatives are needed to reduce these emissions. This study proposes the application of spent diatomaceous earth, a solid waste commonly used in the wine industry as a wine filtration agent, to produce geopolymer mortars.

Geopolymers are inorganic polymers produced from an aluminosilicate precursor and activated by an alkaline solution [4]. They have been studied as alternatives to cement in mortars and concretes. In this work, the geopolymer mortars were produced using spent diatomaceous earth and alumina as precursors, with a Si:Al ratio of 2:1. The activating solution was prepared with sodium hydroxide (NaOH) solution varying the concentration in 10 and 12 M, and sodium silicate in a mass ratio of 1:2, by mixing both with a magnetic stirrer for 10 minutes. Then, this activating solution was mixed with the precursors and distilled water in a standardized paddle mixer. After that, this geopolymer fluid was mixed with sand in a proportion of 1:3:0,85 (geopolymer:sand:water) in the same equipment.

After all the previous steps, the mortar was poured into molds of 40×40×160 mm. The curing process consisted of letting the samples in an oven at 40 ºC for 7 days, demolding them on the fourth day. Subsequently, compressive and bending tests were conducted, and the results are shown in Table 1. Sample G_10M was prepared with a NaOH solution of 10M, and sample G_12M with a solution of 12M.

The results show that using a higher concentration of sodium hydroxide increases compressive and flexural strength. It confirms the literature, as increasing the pH with higher concentrations of NaOH increases the dissolution and solubility of aluminosilicate precursors and provides positive ions to counterbalance the negative charge of the aluminate group [5]. Furthermore, according to the European Standard EN 998-1, with these strengths, both mortars can be defined as class III mortars [6].

Table 1. Mechanical properties of geopolymeric mortars

Sample	Compressive strength after 7 days (MPa)	Flexural strength after 7 days (MPa)
G_10M	4,35	3,11
G_12M	4,46	4,00

Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2020). This work is also a result of the project "BacchusTech - Integrated Approach for the Valorisation of Winemaking Residues" (POCI-01-0247-FEDER-069583), supported by the Competitiveness and Internationalization Operational Programme (COMPETE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

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A computer vision approach in identifying foam consolidation

Edgar Silva-Santos[1,*], **Filipe Teixeira**[1], **Joana Lia Ferreira**[2], **M. Natália D. S. Cordeiro**[1]

[1]LAQV-REQUIMTE, Faculdade de Ciências da Universidade do Porto, Porto, Portugal
[2]LAQV-REQUIMTE, NOVA Faculty of Science and Technology | FCT NOVA, Lisboa, Portugal
**up201801941@edu.fc.up.pt*

Heritage preservation is a delicate and precise job due to the irreplaceable nature of the items to be restored. As such, the importance of studies of restoration processes in mock-ups are a fundamental part of these endeavours [1].

As the use of plastic foams in artworks increases so does the need to find more efficient and more sustainable methods for these materials' preservation. Foam consolidation processes are common ground in the heritage preservation field [1]–[3]. Still, efforts are being made to ensure that these methodologies become greener and more sustainable. To help achieve this, supercritical CO_2 based technologies are being used in foam consolidation [4].

Since testing and evaluating is a complex and laborious process, this work proposes a method for the evaluation of foam consolidation using Machine Learning methods for computer vision in microscope captured images. This way, we hope to achieve a method for evaluating the successful consolidation of a given foam, and in the future, finding the best consolidate through minimal trial and error. To minimise the number of samples produced in the lab, subsampling was used to ensure enough images for the modelling to have viable results. Additionally, a leave-one-out cross-validation similar method was employed to ensure that the maximum number of samples was used in the training set.

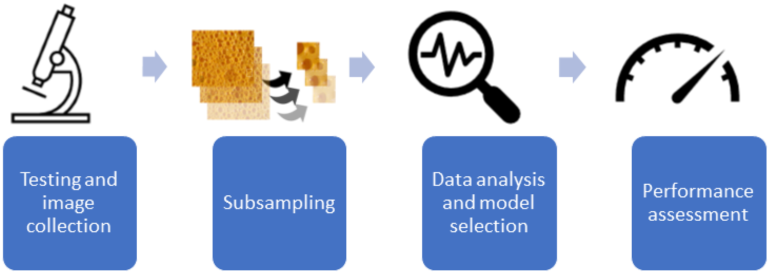

Fig.1. Scheme of the process through image collection up to model deployment.

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New functionalized alginate aerogel materials as potential removal agents of diclofenac in water

A. B. Paninho[a], **T. Rodrigues**[a], **M. Bernardo**[a], **I. Matos**[a], **M. H. Casimiro**[b], **P. Santos**[b], **L. Ferreira**[b], **M. G. Ventura**[a]*

[a] LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10,
Bobadela LRS, 2695-066, Portugal
* *mm.ventura@fct.unl.pt*

Alginate is a natural polysaccharide biopolymer mainly derived from brown algae and consists of α-L-guluronic acid and β-D-mannuronic acid (M) residues, linearly linked by 1,4-glycosidic linkage [1]. Due to its biodegradability, low cost, non-toxicity, and stability it is an attractive candidate for aerogel production [2]. In this work, modified alginate aerogels were prepared from sodium alginate hydrogels graft copolymerization with 2-(Methacryloyloxy)ethylmethylammonium chloride (Fig. 1). The graft copolymerization was promoted via chemical and gamma irradiation approaches. The as prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM), and Thermogravimetric Analysis (TGA).

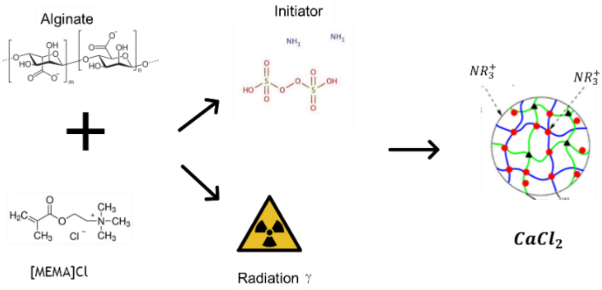

Fig. 1. Schematic representation of the modified alginate aerogels preparation from sodium alginate hydrogels graft copolymerization with 2-(Methacryloyloxy)ethylmethylammonium chloride.

The resultant modified aerogels were then applied for the adsorption of diclofenac sodium, a typical non-steroidal anti-inflammatory drug, from an aqueous solution. The introduction of - (NR3+) groups on aerogels increases diclofenac adsorption capacity which is more evident for the aerogel grafted via gamma irradiation [3]. The modified aerogel in this way exhibited an adsorption capacity of 292.7 mg g^{-1}. The adsorption kinetic studies display adsorption to be the pseudo-second-order rate model. The adsorption isotherm of diclofenac for this aerogel was best fitted by the Freundlich isotherm equation. From the results, it was concluded that the modified aerogels are promising materials for the separation and preconcentration of diclofenac in aqueous solutions.

Acknowledgments

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Inventory of Best Available Techniques candidates for Bioenergy with Carbon Capture, Storage and Utilization

Ignacio Baneres Escribano*, Shoeib Faraji Abdolmaleki, Vaisakh Yesodharan, Pastora M. Bello Bugallo*

TECH-NASE, Department of Chemical Engineering, Universidade de Santiago de Compostela, Avda. Lope Gómez de Marzoa s/n 15782, Santiago de Compostela, España
**e-mail: ignacio.baneres@rai.usc.es; pastora.bello.bugallo@usc.es*

In the future, fuel power generation fitted with Carbon Capture Storage and Utilization (CCSU) is a pivotal part of the transition to net-zero CO_2 emissions. It is a technique for avoiding climate change and limiting global temperature rise. Nowadays, there are some operational facilities of this type in the world, will be a focus for deploying the commercial CCSU in the coming years. The Bioenergy with Carbon Capture Storage and Utilization (BECCSU) techniques, captures emissions from bioenergy plants, is widely used in climate change scenarios. The European Union proposed to lead significant benefits to the environment and human health by reducing harmful industrial emissions across the EU through better application of Best Available Techniques (BAT). The European Integrated Pollution Prevention and Control Bureau (EIPPCB) of the European Commission's Joint Research Centre prepares and revises BAT Reference Documents (BREFs). However, there is no special BREF for those energy sectors that employ BECCSU. Therefore, this study aims to develop a BAT inventory through the existing BREFs and available literature on carbon clean technology. Technical, environmental, and economic data are assessed qualitatively and quantitatively, which considering sector analysis, process identification, environmental aspects, and evaluating inventory of candidates. This study could be part of the EU's inquiries into more sustainable sectors and the application of updated directives. The approach used by IPPC philosophy for sustainable sectors and BAT utilization is explained in the framework of this research.

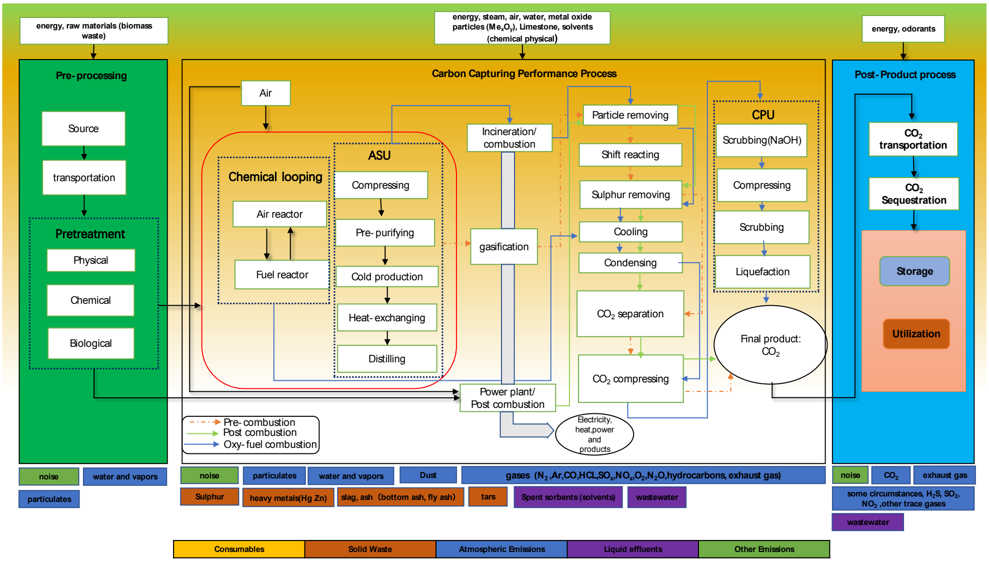

Fig.1. Flow diagram for BECCSU and environmental aspects, including inputs (energy, raw material, water, etc.) and outputs (effluents, emissions, noise, etc.)

Distribución de metais traza en perfís de solos urbanos de Santiago de Compostela

María Roo[1,*], Cecilia Herbón[1], María Teresa Barral[1], Xabier Pontevedra-Pombal[1], Eduardo García-Rodeja[1], Remigio Paradelo[1]

[1]Departamento de Edafoloxía e Química Agrícola, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, España
**maria.roo@rai.usc.es*

Os solos son un compoñente importante dos ecosistemas urbanos, pero as súas funcións poden verse afectadas negativamente debido á acumulación de contaminantes inorgánicos como os metais pesados. Neste traballo analizáronse as concentracións de Pb, Cu, Zn, Ni e Cr en perfís de seis solos da cidade de Santiago de Compostela, tres deles formados en condicións naturais e tres formados sobre materiais transportados e/ou alterados por actividades humanas. Para a análise de metais totais realizouse unha dixestión ácida axudada por microondas de 0,5 g de solo con 3 ml de HF e 9 ml de HNO_3 a 180ºC, seguindo o método EPA 3052 [1]. Os solos urbanos estudiados presentan concentracións variables dos cinco metais traza analizados e diferentes patróns de distribución en profundidade. A concentración de Pb oscilou entre 40-175 mg kg^{-1}. As concentracións de Cu foron moi variables (na maioría dos casos entre 1-70 mg kg^{-1}, cun máximo de 270 mg kg^{-1} nun dos solos artificiais). O contido de Zn variou entre 30-140 mg kg^{-1} e o de Ni entre 12-120 mg kg^{-1}, mentres que a concentración de Cr nos seis solos atopouse nun rango de 4-130 mg kg^{-1}. En dous dos solos naturais as concentracións dos metais traza mostran unha tendencia clara a descender en profundidade, o que suxire que o aporte procede da contaminación do entorno. No outro solo natural, formado sobre anfibolitas, esta tendencia só se cumpre para o Pb, mentres que o Cu, Zn, Ni e Cr aumentan en profundidade, xa que a súa orixe atópase principalmente no material de partida. Polo contrario, en ningún dos tres solos formados sobre materiais transportados se observou unha tendencia clara na distribución dos metais en profundidade.

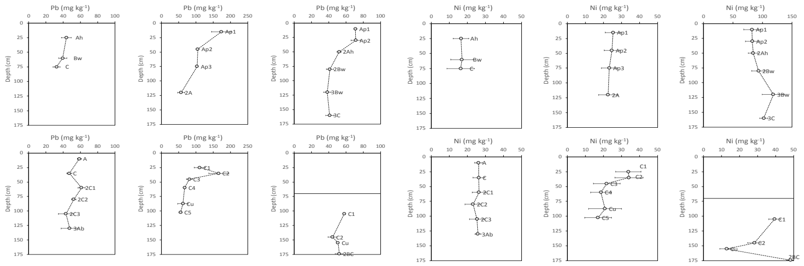

Figura 1. Distribución en profundidade de Pb e Ni nos seis perfís.

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Influence of mercury from wildfires on mussels: a preliminary study in the Galician estuaries

Sofía Lérida Medina*, **Francisco Lopez Ahinara, María Lage Díaz, Vaisakh Yesodharan, Pastora M. Bello Bugallo***

TE-NASE Research Group, Department of Chemical Engineering, Universidade de Santiago de Compostela, Avda. Lope Gomez de Marzoa s/n. Campus Vida, 15782 Santiago de Compostela, Spain
**e-mail: sofia.lerida@rai.usc.es, pastora.bello.bugallo@usc.es*

Wildfires have a direct and indirect impact on estuarine benthic habitats. Due to climate change, megafires are a new and concerning threat to coastal ecosystems [1]. Mercury (Hg) mobilization and accumulation in the environment is directly related to forest fires which affect ecosystem functioning, community composition, behavior, reproduction, and survival of estuarine species. Forest fires could cause MeHg concentrations in fishes to exceed guidelines that protect the health of fish-eating birds and mammals, including humans [2]. The objective of this work is to expand the knowledge on how the mercury that reaches the Galician estuaries due to forest fires affects the aquatic organisms. For this, a preliminary study is carried out through system dynamic using a validated model.

Through a bibliographic search, this work presents an analytical review of the existing works related to the problem of estuarine habitats affected by mercury from forest fires. The elaboration of the state of the art allows us to know the current situation of research and to obtain the data used to implement the model. Our results provide a baseline for in-depth empirical studies and analysis of the actual concern of this issue, as well as encouraging the development of future preventive measures. This study is the first to demonstrate through a dynamic model the impacts of the Hg from wildfires on the estuarine habitat.

Further studies on the impact of Hg from forest fires on estuaries and coastal areas should be carried out to develop our understanding of the results obtained by modelling. Future experiments should investigate how the increase of Hg due to forest fires affect the ecosystem in the long term, considering that fires occurrence is predicted to get increased.

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Vanadium Redox Flow batteries and their effect on grid stability

Sofía Lérida Medina [*1], **Mohammad A. Bany Issa** [1], **Josefa Salgado Carballo**[2], **Pastora M. Bello Bugallo**[*1]

[1]TE-NASE Research Group, , Universidade de Santiago de Compostela, Avda. Lope Gomez de Marzoa s/n. Campus Vida, 15782 Santiago de Compostela, Spain
[2]Department of Applied Physics, Universidade de Santiago de Compostela, Rúa Xosé María Suárez Núñez, s/n. Campus Vida, 15782 Santiago de Compostela, Spain
*e-mail: sofia.lerida@rai.usc.es, pastora.bello.bugallo@usc.es

The energy transition, understood as the major replacement of the energy mix towards a stable, decarbonized one based on renewable energies and energy storage, is one of the most huge and important worldwide challenges. The grid-level energy storage system, especially batteries, is crucial to maintaining a balance between power generation and consumption during the electrical energy transformation process [1, Because of their quick response, modular design, and flexible installation [3], vanadium redox flow batteries (VRFBs) stand out among other battery technologies because of their excellent energy efficiency, lengthy cycle life, safety, environmental friendliness, and good performance [1, 2]. This viewpoint has a detailed analysis of the characteristics of VRFBs, including their operation mechanism, battery design and construction, and benefits and drawbacks [3]. The effectiveness of VRFBs used with grid-level energy storage systems is also evaluated in terms of the following grid services: frequency and voltage regulation, power management, and incorporation of renewable energy sources (RES), in order to shed light on the advancement of grid-level energy storage systems.

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Determination of bioactive compounds from cork powder extracts by high-performance liquid chromatography

Cláudia Pinto[1], Sara Cravo[1,2], Carlos Afonso[1,2], Joana Rocha e Silva[3], Honorina Cidade [1,2], Maria Elizabeth Tiritan[1,2,5*], Isabel F. Almeida[5,6]

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal
[3]Dimas & Silva, Lda. Industry, Rua Central de Goda 345, Mozelos, Portugal
[4]TOXRUN – Toxicology Research Unit, University Institute of Health Sciences, CESPU, CRL, Portugal
[5]UCIBIO – Applied Molecular Biosciences Unit, MedTech, Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal
[6]Associate Laboratory i4HB - Institute for Health and Bioeconomy, Faculty of Pharmacy / Faculty of Medicine, University of Porto, Porto, Portugal
** beth@ff.upt;* dedicado pela autora à memória do professor Costa Lima

Nowadays, circular economy is a widely present concept in pharmaceutical and cosmetic industry mainly due to consumer's awareness and demand for more sustainable products, which is demonstrated by the attempt to upcycle by-products from agro-industrial waste to produce eco-friendly ingredients [1].

Quercus suber is a tree widely present in southern Mediterranean countries whose unique outer bark, cork, is an important raw material with multiple applications. However, the amount of waste generated in cork production and transformation processes is one of the main problems intrinsic to the cork industry, which adds the need to mitigate this scenario [2]. Cork powder is considered the major cork by-product once it comes from practically all the transformation processes. Thanks to its high heating value, it is mainly reused in industry for energy production but can also be used as biosorbent, filling agent in cork stoppers or incorporated into agglomerates [3]. Nevertheless, several studies have been considering this by-product as a source of bioactive compounds, especially phenolics compounds, with reported antioxidant activity and putative application in a variety of skin care products [4].

This work reports the determination of several bioactive compounds from different cork powder extracts by high-performance liquid chromatography with UV detection. A green analytical method was optimized, in order to improve the sustainability in chemical analysis, and validated according to the international guidelines for quantification of eleven bioactive compounds in alcoholic and hydro-alcoholic extracts of cork powder for further incorporation into pharmaceutical and cosmetic formulations.

Acknowledgments

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Sustainable Use of Batteries According to the Electricity Prices: Energy Management and Lifespan

María Lage-Díaz[1*], Zaid A Al Muala[1], Daniel Sansó-Rubert Pascual[2], Josefa Salgado Carballo[3], Pastora M. Bello Bugallo[1*]

[1] TECH-NASE Research Group, School of Engineering (ETSE), Universidade de Santiago de Compostela, Avda. Lope Gomez de Marzoa s/n 15782, Santiago de Compostela, Spain
[2] Department of Legal and Political Science, Universidad Europea de Madrid, C/ Tajo, s/n 28670, Villaviciosa de Odón, Spain
[3] Department of Applied Physics, Universidade de Santiago de Compostela, Rúa Xosé María Suárez Núñez, s/n. Campus Vida, 15782 Santiago de Compostela, Spain
**e-mail:* maria.lage.diaz@rai.usc.es, pastora.bello.bugallo@usc.es

With the increase in electricity prices and the implementation of demand response (DR) programs to contribute to energy security, the energy storage system (ESS) plays a critical role in reducing the electricity bill and contributing to grid stability [1],[2].

In the residential sector, as installing ESS such as batteries has a cost, and the electricity price in Spain fluctuates hourly, the battery energy management system (BEMS) is crucial for efficient battery usage (economically & safely).

This work shows how to manage battery energy usage efficiently based on electricity prices in Spain, and battery investment cost, together with the battery state of charge (SOC), charge power limit (CPL), and discharge power limit (DPL), in order to sustain its lifespan and reduce its energy losses while reducing bill costs.

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BIOQUÍMICA Y BIOTECNOLOGÍA

Development of an enzymatic biosensor based on boron-doped diamond surface

Bernardo L. Tavares[1,*] **, Diogo R. Fernandes** [1] **, Leandro R. Freitas** [1] **, Valéria C. Ebinuma-Santos** [2] **, João C.F. Nunes** [2] **, Márcia C. Neves** [1] **, Ana V. Girão** [3] **, Miguel A.C. Neto** [3] **, Ana P.M. Tavares** [1]

[1] Chemistry Department, CICECO–Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
[2] Department of Engineering of Bioprocesses and Biotechnology, School of Pharmaceutical Sciences, São Paulo State University (UNESP), Brasil
[3] Department of Materials and Ceramics Engineering, CICECO—Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
**bernardo.tavares@ua.pt*

L-asparaginase (ASNase) is an enzyme used as an anti-leukemic biopharmaceutical that acts in the reduction of L-asparagine (Asn), a compound that favors tumoral growth in patients with acute lymphoblastic leukemia (ALL).[1] Thus, the control of depletion levels of Asn in patients treated with ASNase is important. Since the methods currently used for this purpose are sophisticated, time consuming and expensive, there is a continuous effort to develop new alternatives.[2] In this regard, ASNase-based biosensors have been developed for the quantification of Asn.[3] Due to its unique properties, diamond has been used as an ideal platform for the development of a new generation of superior biosensors.[4,5] This work aims at the immobilization of ASNase on the surface of temperature sensitive O2 and NH3 plasma functionalized polycrystalline CVD diamond, using the HFCVD technique, on monocrystalline silicon, to allow the development of a biosensor for the treatment monitorization of ALL. Several microcrystalline diamond films were deposited, in which the ASNase was immobilized by physical adsorption. The success of the enzyme attachment was confirmed through activity tests. The diamond surface before and after enzyme immobilization was characterized by FTIR-ATR, SEM, RAMAN and OCA allowing to further understand the conditions in which the enzyme was immobilized. Concluding, the obtained results encourage the development of the proposed diamond-based thermal biosensor.

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The effect of calcium in the fermentation of white cabbage and salicornia

Patrícia Pires-Cabral[1], Paula Pires-Cabral[1], Helena Mira[2], Célia Quintas[1]

[1]Universidade do Algarve, Instituto Superior de Engenharia, MED-UAlg Campus da Penha Faro, Portugal
[2]Instituto Politécnico de Santarém, Escola Superior Agrária, Quinta do Galinheiro - S. Pedro, Santarém, Portugal, CIEQV - Centro de Investigação em Qualidade de Vida, Avenida Dr. Mário Soares, Rio Maior, Portugal
**cquintas@ualg.pt*

The objective of the present investigation was to study the effect of the addition of calcium chloride in the fermentation of white cabbage (*Brassica oleracea*) and the halophyte *Salicornia ramosissima*, as well as on the sensorial properties of the fermented final products.

Two experiments were performed: A- cabbage with salt and salicornia (80 g of cabbage, 0.4 g of NaCl and 24 g of salicornia) and B- cabbage with salt, salicornia and calcium chloride (80 g of cabbage, 0.4 g of NaCl and 24 g of salicornia, and 1,28 g $CaCl_2$).

During the fermentation period, the populations of lactic-acid bacteria (LAB), coliforms and fungi and physicochemical characteristics (pH, total acidity, hardness, mineral contents) were studied.

A reduction of the pH values (A-4,07±0,01; B-3,58±0,01) and an increase in the acidity values (A-0,70±0,01%; B-0,77±0,01%) were registered during the fermentation period. An exponential growth of the LAB populations was observed in both experiments and at the end of the fermentations a slight decrease of these bacteria was noticed (A-6,0±1,0;B-5,5±0,1 Log UFC/g). During the first week there was a decline of fungi and the coliform populations disappeared after about 12 days of fermentation. *Escherichia coli* and *Salmonella* were not detected in the final products. The utilization of calcium chloride as an ingredient in the fermentation of white cabbage and salicornia, resulted in the final fermented cabbages with an increased hardness (A-4,4±0,7; B-6,3±0,1 N) but having analogous phisicochemical, microbial and sensorial properties.

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Development of a novel phagomagnetic separation protocol coupled with isothermal DNA amplification for a rapid *Campylobacter* detection

Cláudia Maciel[1,2], Nádia F.D. Silva[2], Rui Meneses[1], Paula Teixeira[1], Júlia M.C.S. Magalhães*[2]

[1]Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal.
[2]REQUIMTE/LAQV, Department of Chemical Engineering, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal
**up228772@up.pt*

Campylobacter spp. are recognized as the leading cause of bacterial-associated gastroenteritis worldwide, imposing a burden on public health. In Europe, *Campylobacter jejuni* is the most commonly reported species, representing 88.1% of the confirmed human cases in 2020 [1]. The conventional microbiological procedures for the detection of *Campylobacter* in food matrices, albeit reliable and accurate, are laborious and time-consuming. (Bacterio)phages immobilized onto magnetic particles have emerged as promising bio-probes to capture and pre-concentrate *Campylobacter* from samples. The subsequent conjunction with isothermal DNA amplification techniques, presenting a well-documented potential as robust analytical tools, may provide an accurate, highly specific and cost-efficient routine screening method for the presumptive presence of the bacterium.

The purpose of the present work was to develop a novel bacteriophage-based magnetic separation protocol, coupled with loop-mediated isothermal amplification (LAMP) or recombinase polymerase amplification (RPA) for a specific and rapid *C. jejuni* detection. The performance of polyethyleneimine surface modified magnetic particles biofunctionalized with lytic phage Los1 (Los1-MP) was optimized for *C. jejuni* capture. An in-depth investigation of the main parameters governing the bacterial capture efficiency (CE) was performed through the evaluation of the MPs amount (32 - 240 µg), temperature (11- 41 °C), incubation time (10 - 60 min), pH value (5 - 7) and divalent cations (2 mM Ca^{2+}, Mg^{2+}). The sensitivity of the phagomagnetic separation protocol was determined using distinct bacterial loads (10^2 -10^6 CFU mL^{-1}), while its selectivity was assessed against a panel of Gram-negative bacteria.

Concerning the Los1-MP amount, a concomitant improvement was observed in *Campylobacter* CE with the increase in the quantity of particles up to 160 µg. The optimum incubation time was established to be 20 min. The pH, along with the incubation temperature, was unveiled to be a pivotal parameter concerning the *Campylobacter* capture and the highest efficiency occurred at 41 ºC and pH 5. The divalent cations inclusion significantly ($p < 0.05$) enhanced the *Campylobacter*-phage Los1 interaction. Los1-MP was found to be highly sensitive, presenting a separation limit below 10^2 CFU mL^{-1}. Regarding selectivity, the CE of non-target bacteria was residual. The isothermal amplification technique presented high specificity and a remarkable capability of on-site nucleic acids detection.

Herein, the feasibility of utilizing Los1-MPs towards the rapid and selective enrichment of *Campylobacter* in food matrices was demonstrated. The study highlighted that the bacterial capture efficacy was not only dependent on the phage immobilization (tail-up/head-down), since critical parameters also dictated the *Campylobacter*-Los1 interaction. Moreover, the proposed combined approach may provide a reliable molecular-based surveillance tool for food safety analytical services and public health authorities. This methodology could be of utmost importance to comply with food safety standards.

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Innovative phagomagnetic-assisted isothermal DNA amplification system for endpoint electrochemical detection of *Listeria monocytogenes*

Cláudia Maciel[1], Nádia F.D. Silva[2], Paula Teixeira[1], Júlia M.C.S. Magalhães*[2]

[1]Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal

[2]REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal

**up228772@up.pt*

Listeriosis is an opportunistic disease caused by the foodborne bacterial pathogen *Listeria monocytogenes* (*Lm*). This infection is rare (in 2020, 1876 human cases were reported in the EU [1]), but it is frequently associated with high hospitalization and mortality rates (20-30%) [2]. *Lm* tolerates hostile environments, in which low temperatures and osmotic stresses may be found. Ready-to-eat foods (RTE) are often the source of listeriosis as their long shelf-life is conducive to *Lm* growth and are commonly consumed without any additional thermal processing. The Regulation (EC) 2073/2005 of the European Commission establishes that *Lm* levels in RTE must be below 100 CFU g^{-1} at any point during the shelf-life or absent in 25 g of RTE foods able to support the growth of the bacterium [3].

This work proposes a rapid method for *Lm* detection resorting to the lytic (bacterio)phage P100, capable of infecting, replicating, and specifically lysing viable *Lm* cells, coupled to loop-mediated isothermal amplification (LAMP) of the DNA released from P100-captured host cells. For this purpose, the phage was physically immobilized on magnetic particles under favourable electrostatic conditions in a likely head-tail orientation and the phage-magnetic probes were utilized to capture and pre-concentrate *Lm* cells from the milk samples.

Concerning LAMP, in order to achieve high sensitivity, four core primers targeting six specific regions of the virulence gene *prfA* (clustered in the *Listeria* Pathogenicity Island 1) were designed. The LAMP reaction system was optimized regarding the concentration ratio of the external and internal primers, along with the *Bst* DNA polymerase and the co-factor concentrations. The developed method sensitivity, specificity and selectivity were evaluated. The LAMP assay performance was validated in milk samples, spiked with *Lm* (10^2 CFU mL^{-1}), and the phagomagnetic captured bacteria were thereafter lysed with phage P100, being the released DNA LAMP-amplified.

The optimized LAMP procedure proved the capability to detect the five *L. monocytogenes* serotypes (1/2a, 1/2b, 1/2c, 4b and 4c) evaluated. Concerning specificity, cross-reactivity was not observed for other *Listeria* species and non-target strains of both Gram-positive and Gram-negative bacteria. This novel assay targeting *prfA* presented a limit of detection of 10 fg mL^{-1}. The proposed method demonstrated excellent concordance with the golden standard PCR technique. The performance of LAMP in spiked milk samples and pure bacterial cultures was comparable.

Electrochemical detection resorting to methylene blue was also used as the endpoint detection of the LAMP products. The optimized assay coupled with endpoint electrochemical detection demonstrated to be a promising approach for the detection of viable *Lm* cells in contaminated food samples.

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IDENTIFICACIÓN DE NOVOS INHIBIDORES DO RECEPTOR DE COLÁXENO GPVI MEDIANTE UN ENSAIO FENOTÍPICO

Francisco José Rodríguez del Río[1], Sara Troitiño[1], Irene Izquierdo[1], Gema Prieto da Cuña[1], Nuria Gómez-Romero[1], Lidia Hermida-Nogueira[1], Eduardo Domínguez[2], María I. Loza[2], Ángel García[1]

1 Platelet Proteomics Group, Center for Research in Molecular Medicine and Chronic Diseases (CIMUS), Universidade Santiago de Compostela and Instituto de Investigación Sanitaria de Santiago (IDIS), Santiago de Compostela, Spain. 2 Innopharma Screening Platform, BioFarma Research group, Center for Research in Molecular Medicine and Chronic Diseases (CIMUS), Universidade de Santiago de Compostela, Santiago de Compostela, Spain.
franciscojose.rodriguez.delriio@rai.usc.es

Antecedentes: Os medicamentos antiplaquetarios actuáis, están asociados con frecuencia a un risco significativo de hemorraxia, comprometendo a función plaquetaria. A procura de novos medicamentos antiplaquetarios sen alterar en gran medida a hemostasia é una necesidade imperante. A glicoproteína VI (GPVI), receptor do coláxeno, é unha diana prometedora, xa que únicamente se expresa en plaquetas e megacariocitos, e o seu bloqueo tamén inhibe a formación de trombos. [1]

Obxectivo: Identificar novas moléculas capaces de inhibir o receptor GPVI mediante un cribado fenotípico e que poidan progresar a ensaios clínicos como novos medicamentos antiplaquetarios.

Materiais e métodos: Os ensaios fenotípicos de liberación de calcio foron empregados para identificar inhibidores da agregación plaquetaria a través da modulación do receptor GPVI. O ensaio "label-free dynamic mass redistribution" (DMR), confirmou a unión do ligando co receptor. Series de derivados das moléculas foron sintetizadas empregando una estratexia de farmacomodulación. Os estudos funcionais basearonse na agregación plaquetaria e "spreading". Os ensaios de viabilidade empregando citometría de fluxo foron usados para evaluar a posible toxicidade dos ligandos.

Resultados: 2 moléculas mostraron eficacia ao inhibir a liberación intracelular de calcio e a agregación plaquetaria mediante a modulación do receptor GPVI, SIL-ENA e SEDN2 (pendentes de patente). SEDN2 amosou os resultados mais potentes en canto a inhibición e foi empregada como estructura de partida para a síntese de 19 moléculas semellantes. 2 destos derivados mostraron un potente efecto inhibitorio e priorizáronse, xunto con SEDN2, para estudos preclínicos. Os candidatos non mostraron efectos tóxicos a doses micromolares, amosando inhibición significativa da agregación e da adhesión.

Conclusións: Novos ligandos do receptor GPVI con efecto antiplaquetario foron identificados e priorizados empregando cribados fenotípicos e estudos funcionais.

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CATÁLISIS Y FOTOCATÁLISIS

Synthesis of Cu_2ZnSnS_4 by hydrothermal method and its application as Congo Red photocatalyst.

Paula Salazar[1,*], **Rodrigo Henríquez**[2], **Pablo Zerega**[3]

[1,2,3]Laboratorio de Electroquímica, Instituto de Química, Facultad de Ciencias, PUCV, Av. Universidad 330, Valparaíso, Chile.

**paula.salazar@pucv.cl*

The textile, food and pharmaceutical industries are expanding daily worldwide, they are located within the most polluting industries due to the fact that wastewater is discharged into watercourses with high concentrations of dyes and traces of drugs. Many of these compounds are stable to light and biodegradation, being considered as emerging organic contaminants [1]. Advanced oxidation processes (AOPs) emerge as an effective alternative for the removal and elimination of this type of contaminants. Heterogeneous photocatalysis has been extensively studied as it is an efficient, low-cost and durable method. As the main photocatalyst, TiO_2, has been used for the degradation of a large number of dyes and drugs. The disadvantage of TiO_2 is its absorption in the UV region of the solar spectrum [2]. On the other hand, quaternary chalcogenides based on Cu_2ZnSnX_4 (X = S, Se) are a possible alternative due to their close band gap (ca. between 0.8 to 1.5 eV depending on the phase considered), low cost, abundance of its constituent elements in the earth's crust and its low toxicity. As a photocatalyst, Cu_2ZnSnS_4 (CZTS) has shown good results in the treatment of some emerging organic pollutants, but studies are scarce [3].

The objective of this research was to synthesize Cu_2ZnSnS_4 (CZTS) through of a low-cost hydrothermal method and evaluate it as a potential photo-catalyst in the photo-degradation process of Congo Red.

The synthesis of the nanoparticle in suspension and film onto fluorine doped tin oxide coated glass (FTO) was carried out using a mixture of: 2 mmol $CuCl_2$, 1 mmol $ZnCl_2$, 1 mmol $SnCl_2$ and 4 mmol CH_4N_2S in a Teflon reactor at 180°C for 72 h. Characterization was performed through scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV VIS spectroscopy. Photo-degradation monitoring was carried out employing a UV VIS spectrophotometer.

Through the analysis of the UV VIS spectra (see Fig. 1), it has been possible to determine that the photodegradation process has a yield of 90.2% with only 60 minutes of exposure.

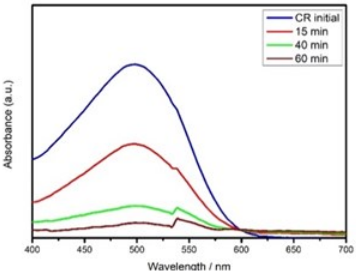

Figure 1. Molecular absorption spectrum obtained in the photo-degradation of CR.

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Síntese de nanopartículas de óxido de ferro III dopadas e não dopadas com rutenio utilizando extrato hidro-alcoólico da folha de *Syzygium cumini* (L.) Skeels (jamelão)

Davi Souza Ferreira[1,*], **Naldirene do Nascimento Fonseca[1]**, **Adriana das Mercês Pereira Ferreira[1]**, **Paulo Roberto Garcês Gonçalves Júnior[1]**, **José Hilton Gomes Rangel[1]**

[1]Programa de Pós-graduação em Química (PPGQ/IFMA), Instituto Federal de Educação, Ciência e Tecnologia do Maranhão – IFMA, Campus São Luís Monte Castelo. Avenida Getúlio Vargas, nº04, Monte Castelo, 65030-005, São Luís, Brasil

**davi.souza@acad.ifma.edu.br*

Materiais nanoestruturados tais como Magnetita (Fe_3O_4), maghemita (γ-Fe_2O_3) e hematita (α-Fe_2O_3) têm atraído considerável interesse devido suas propriedades físicas promissoras, como momento magnético aprimorado, biocompatibilidade e estabilidade química [1, 2]. Dentre os metódos químicos para obtenção de óxidos de ferro, podemos citar as rotas sol-gel, co-precipitação e hidrotermal. No entanto, atualmente, busca-se a obtenção das nanopartículas de óxido de ferro por meio de uma abordagem que seja mais benéfica ao ambiente visando minimizar o efeito tóxico de produtos químicos e aumentar a biocompatibilidade do reagente, tornando-o mais verde[1].

Assim, este trabalho visou sintetizar nanoparticulas de óxido de ferro III dopadas com rutênio (Fe_2O_3-Ru) via síntese verde utilizando extrato hidro-alcoólico da folha de *Syzygium cumini*(L.) Skeels (jamelão), $Fe(NO_3)_3.9H_2O$ e $Cl_3Ru.xH_2O$ como precursores metálicos. O Fe2O3 [3] pertence ao grupo espacial R-3c (nº 167), apresenta célula unitária (Figura 1) com parâmetros de rede a = b = 5,03550 Ǻ, c = 13,74710 Ǻ, α = β = 90º, γ = 120º. Foram testadas duas temperaturas de calcinação. Para identificação da fase cristalina, realizou-se a análise de difração de raio X (DRX).

Os picos observados no DRX correspondem a carta JCPDS 00-033-0664 da fase hematita (α-Fe2O3), no entanto, tem-se uma fase secundária compatível com a fase ortorrômbica de Fe_2O_3 de acordo com a carta JCPDS 01-089-7047 (Figura 2). Podemos concluir que o material calcinado a 650 ºC apresentou maior cristalinidade e que é possível obter nanoparticulas de Fe_2O_3-Ru utilizando extrato da folha de jamelão, de forma simples, barata e benéfica ao ambiente.

Fig.1 Célula unitária de Fe2O3.

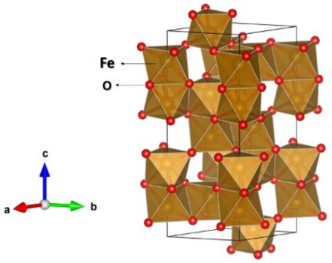
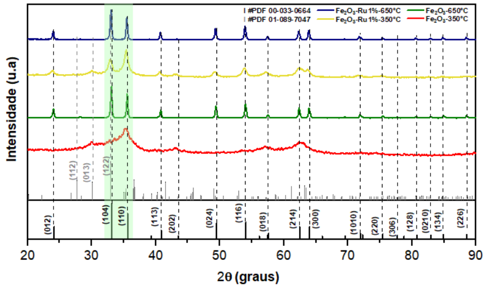


Fig. 2. Difratogramas dos óxidos de ferro sintetizados via síntese verde



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Synthesis of nanostructured organometallo-titania hybrid materials and their application in dye degradation

Janira Herce[1*], **Miguel A. Rodríguez**[1], **Jesús R. Berenguer**[1], **Elena Serrano**[2], **Javier García-Martínez**[2]

[1]Departamento de Química-Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Madre de Dios 51, E-26006, Logroño, Spain.
[2] Laboratorio de Nanotecnología Molecular. Departamento de Química Inorgánica. Universidad de Alicante, Carretera San Vicente s/n, E-03690, Alicante, Spain
*jaherce@unirioja.es

Titanium dioxide (TiO_2) is one of the most promising materials at present due to its wide variety of applications. However, it has some drawbacks due to the high electronic hopping between the valence and conduction bands (or bandgap). To solve this problem and get visible-light active titania, our group has developed an *in-situ* method based on the so-called *Sol-Gel Coordination Chemistry* [1] (Figure 1). For this purpose, two nanostructured organometallo-titania hybrid materials, **[1]-TiO_2** and **[2]-TiO_2**, have been prepared from two Ir(III) complexes: $[Ir(ppy)_2(3,3'\text{-}H_2dcbpy)](PF_6)$ (**1**) [2] and $[Ir(ppy)_2(4,4'\text{-}H_2bicinchoninic)](PF_6)$ (**2**), respectively. These materials have proven to be very stable and effective photocatalysts under visible-light irradiation in the degradation of Rhodamine 6G in aqueous media, showing that the new **[2]-TiO_2** material is three and six-fold effective than **[1]-TiO_2** and a related **complex-free titania**, respectively.

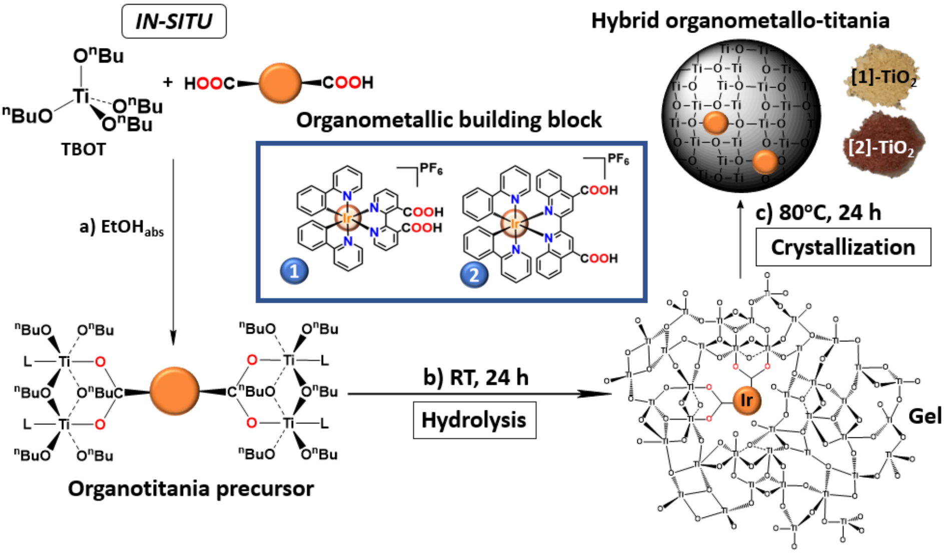

Fig. 1. *In-situ* hybrid materials obtained by *Sol-Gel Coordination Chemistry*.

Acknowledgments

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Iron-based metal organic framework as an active electrocatalyst for water splitting reactions

Aida M. Díez[1,*], **Marta Pazos**[1], **M. Ángeles Sanromán**[1]

[1]CINTECX, Grupo de Bioingeniería y Procesos Sostenibles, Departamento de Ingeniería Química, Campus Lagoas-Marcosende, Universidade de Vigo, 36310 Vigo, Spain
**adiez@uvigo.es*

Metal Organic Frameworks (MOFs) have been lately used due to their fantastic properties such as high stability, high porosity and the possibility of design *ad hoc* modifications [1]. Those properties make them attractive as catalysts [2]. Among the processes to be catalysed, water splitting stands out. This process is based on the generation of H_2 as a renewable and green fuel where a catalyst, in this case, the MOF, promotes the two semi-reactions for overall water splitting: the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER). This latter is the limiting step [2] and consequently, this research was focused on using for the first time the MOF NH_2-MIL-101(Fe) to promote alkaline OER.

NH_2-MIL-101(Fe) was synthesized following a simple hydrothermal method [3] and characterized deeply by XPS, N_2 isotherms and the measurement of the Electrochemical Active Surface Area (ECSA), Electrochemical Impedance Spectroscopy (EIS), TEM, XRD and FTIR. Those analyses demonstrated the stability, crystallinity and high surface and active area of NH_2-MIL-101(Fe).

In terms of OER activity, to begin with, the effect of the catalyst dosage was optimized (Fig. 1). Consequently, 0.25 mg cm^{-2} was set as the optimal dosage, defeating the performance of the raw supporting electrode, Ni foam (NF). Moreover, this MOF performed better than the best reported alkaline OER catalyst, IrO^2 (Fig. 1). Moreover, EIS, Tafel slope and stability tests (10 mA during 100 h and 3000 cycles on the range 0-100 mA) demonstrated a current detriment of less than 5 %. This opens a path for the efficient application of water splitting reactions without unstable, rare and expensive metals.

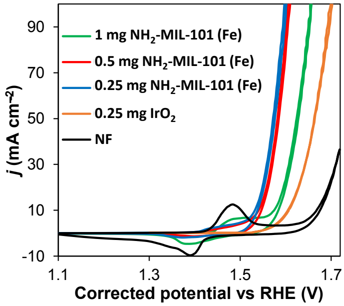

Fig.1. Alkaline OER profiles of NH_2-MIL-101(Fe) at different dosages.

Table 1. Electrocatalyst performance evaluation of the used MOF and control experiences.

Working electrode	**Overpotential (mV)**			**Tafel slope (mv dec^{-1})**
	10 mA	**50 mA**	**100 mA**	
0.25 mg NH_2-MIL-101(Fe)-NF	303	343	367	44.4
0.25 mg IrO_2-NF	380	430	470	71.5
NF	235[a]-430	>480 (36.5 mA)		65.4

[a]Pre-oxidation peak

Acknowledgements
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Sugar cane-derived solid acid catalysts for the production of fuel additives via glycerol esterification

Anna Malaika[1*], Karolina Ptaszyńska[1], Katarzyna Morawa Eblagon[2a, b], Mieczysław Kozłowski[1], José Luís Figueiredo[2a, b]

[1]Adam Mickiewicz University in Poznań, Faculty of Chemistry,
Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland
[2a]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2b] ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto,
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
**e-mail: amalaika@amu.edu.pl*

Carbon-rich materials from biomass-derived carbohydrates have been widely applied in catalysis, adsorbents, and electrodes [1]. Thus, there is a significant interest in eco-friendly and cheap technologies producing these materials, especially from agricultural or industrial wastes. The sugar industry worldwide manufactures large volumes of sugar cane molasses (SCM), mostly used for cattle feed [2]. Alternatively, SCM residue can be used as a renewable resource to produce carbon materials. This approach limits the reliance on fossil-based resources and decreases waste generation while providing additional revenue for agricultural industries.

In the present work, sugar refinery waste (sugar cane molasses, SCM, syrup;) was used as a substrate to produce carbon catalysts containing sulfonic and oxygen functionalities. Two environmentally friendly synthesis approaches were compared: partial carbonisation (PC) and hydrothermal carbonisation (HTC). In the PC method, involving carbonisation and functionalisation in-situ, SCM was heated with the addition of concentrated sulfuric acid at 180 °C for 0.5 h, which resulted in a PC-C-SO_3H sample. Alternatively, a two-step method was applied, involving carbon formation via classical HTC, followed by post-functionalisation. In the HTC, a solution of SCM syrup was heated at 180 °C under autogenous pressure for 8h, which resulted in HTC-C. Subsequently, HTC-C was functionalised by treatment with concentrated sulfuric acid, resulting in the HTC-C-SO_3H sample. The prepared solid acid catalysts were characterised and evaluated in glycerol acetylation to acetins, i.e., important fuel additives.

It was found that both preparation methods used (i.e., HTC and PC) were convenient techniques for upgrading molasses to high-value carbonaceous products. Both these processes formed hydrochars with abundant functional groups. However, the PC-C sample showed acidic O- and S-functionalities, whereas HTC-C required additional post-functionalization to anchor the -SO_3H moieties to the carbon surface. The EA results showed that HTC-C-SO_3H and PC-C- SO_3H contained around 30% oxygen and 1.5-2.3% sulfur. According to XPS results, S-functionalities were found on their surfaces, mostly in the form of sulfonic groups. The solid acid catalysts could effectively facilitate the transformation of glycerol to acetins. Both samples showed a very high glycerol conversion (~96% within 1 h) and high yields of di- and triacetins (72-77% after 1 h). However, considering the carbon preparation conditions, the complexity of the preparation method, process feasibility, and environmental impact, PC carbonization was indicated as a promising option for converting sugar wastes to cheap active catalysts.

Acknowledgments

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Green diesel production *via* hydrogen free sustainable catalytic processes

Marta Monteiro[1,2]*, José Marques[2], Luís Álvares Ribeiro[1] and Andreia F. Peixoto[1,2]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, Porto 4169-007, Portugal
[2]INNOVCAT, Rua Nova da Ribela, 220, 4475-710 Maia, Portugal
**martamonteiro13.mm@gmail.com*

Biofuels play a crucial role as a sustainable alternative to the strong dependency of fossil resources and the consequent environmental and economic concerns.[1,2] **Green diesel** is a renewable biomass derivative obtained by the catalytic deoxygenation of vegetable oils (VO), representing a sustainable substitute to mineral diesel, as they have similar physicochemical properties. The hydroconversion (HC) of VO and fats in the presence of high pressure H_2, high temperatures (> 300 ºC) and noble metals-heterogeneous catalysts is currently the most common approach to obtain this biofuel.[3] However the high cost barriers made them unattractive.This work in collaboration with INNOVCAT, aims to develop efficient and robust catalysts using biochar (carbon based material derived from shrimp shell waste)[4] activated and functionalized with transition metals (Ni, Co, Mo) to be used in the catalytic HC of VO into green diesel, using T < 300 ºC and only water and formic acid as alternative source to generate in situ *green* hydrogen avoiding the used of high pressure H_2 derived from fossil resources. Under these conditions it was possible to convert (100 % conversion) linoleic acid (unsaturated free fatty acid-FFA) in other saturated derivatives. The same catalysts were used to HC of other lignocellulosic biomass derivatives and the results will be presented. All the catalysts and products were characterized by SEM-EDS, XPS, FTIR, GC-MS, ^{1}H and ^{13}C NMR, etc.

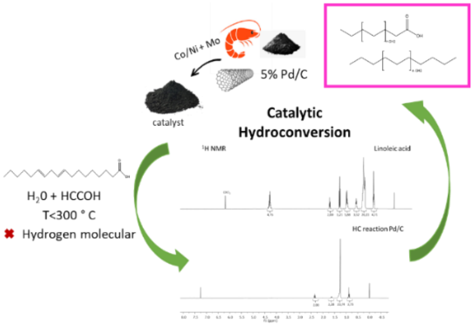

Fig. 1. Schematic illustration of HC reaction of linoleic acid under sustainable conditions.

Keywords: Green diesel, biomass resources, shrimp shell waste, biochar

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CAT29

Development of oxidative catalytic processes in continuous flow chemistry for drug degradation

Diana L. Marques[1,*], Giusi Piccirillo[1], Fábio M. S. Rodrigues[1], Mário J. F. Calvete[1], Mariette M. Pereira[1]

[1]University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, Rua Larga, 3004-535, Coimbra, Portugal
**diana.lourenco.marques@hotmail.com*

Given the increase in antibiotic consumption by human and veterinary medicine, the presence of significant amounts of these drugs in aquatic environments is currently easily detected. Due to their environmental persistence, some bacteria can develop enhanced antibiotic resistance.[1] For this reason, the development of methods applied to the degradation of antibiotics in wastewater became a topic of huge importance in the fight against antimicrobial resistance (AMR).

To this respect, advanced oxidation processes (AOP)s have emerged as a hot topic regarding the development of efficient systems for the degradation of pharmaceuticals in water,[2] of which we highlight the heterogenized porphyrin macrocycles, as reusable catalysts that demonstrate high potential in promoting the generation of reactive oxygen species (ROS)s to oxidize antibiotics in aqueous media.[3,4]

Nevertheless, the implementation of these AOP methods in batch (static) systems becomes impractical in a real-world situation. To overcome this shortcoming, the use of continuous flow processes delivers great potential regarding the transposition from a laboratory scale for application in the treatment of wastewaters, e.g. from hospitals and medical facilities.

Therefore, in this communication we present our achievements in the pioneering development of a metalloporphyrin-based immobilized material, implemented as catalyst for the oxidative degradation of a highly detected antibiotic (trimethoprim), in the presence of H_2O_2 as a non-polluting oxidant, in a continuous flow process.

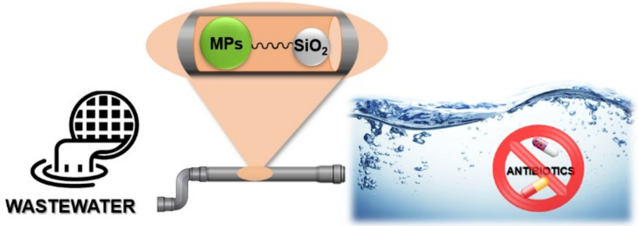

Fig.1. Degradation of antibiotics in hospital wastewater by using metalloporphyrin immobilized in continuous flow.

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Photocatalytic transformation of biomass-derived compounds into valuable products

<u>Marta Monteiro</u>[1,*], Ana Cláudia Santos[2], Bruno Valentim[2], Alexandra Guedes [2], Waldemar Maniukiewicz[3], Andreia F. Peixoto[1,] Iwona Kuźniarska-Biernacka [1]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, Porto 4169-007, Portugal
[2]Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, Porto 4169– 007, Portugal
[3]Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Łódz, Poland;
**martamonteiro13.mm@gmail.com*

The petrochemical products relying on fossil fuels have a critical role in daily life human demands. The conversion of biomass-derived platform compounds into value-added chemicals may replace fossil fuel derivatives. [1] For example, the 5-hydroxymethylfurfural (HMF) is widely recognized as an important bio-platform molecule obtained by dehydration of C5-C6 sugars, with a great potential for the synthesis of many valuable (fine)chemicals including the 2,5-furandicarboxylic acid (FDCA) derivative via selective oxidation. However, the use of harmful stoichiometric oxidants and metal noble based-catalyst make this highly desired process ecological and economical unattractive. [2]

Here we present and discuss the preparation and characterization of new, a tri-component hybrid catalyst composed by coal fly ash char (CFA), chitosan (CS) and TiO_2 semiconductor (CFA@CS@TiO_2). The catalyst was prepared by wet impregnation based on ionic gelation using sodium tripolyphosphate as across-linking agent and coal fly ash char by method described in [3]. For comparison reasons a CFA@CS material was also prepared, and all the materials (TiO_2, CFA, CFA@CS and CFA@CS@TiO_2) were characterized via SEM-EDS, FTIR, Raman, XFR and XRD. The methods confirmed that CFA was successfully coated by CS forming the CFA@CS and also efficient immobilization of TiO_2 forming the CFA@CS@TiO_2.

All materials were tested as photocatalysts in oxidation of aqueous solution of HMF using a quartz reactor and the reaction medium was illuminated by low power UV-A lamp (15 W) during 300 min. The catalytic reactions were monitored by high performance liquid chromatography. To optimize the catalytic conditions, the effect of substrate/catalyst ratio was tested. The fastest HMF oxidation (nearly total HMF conversion in 300 min) was obtained for 100 mL of 4.04×10^{-4} M of substrate in the presence of 10 mg of photocatalyst.

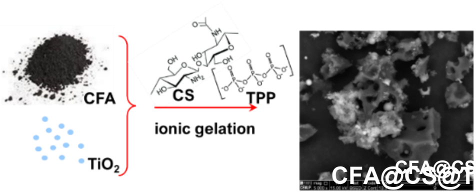

Fig. 1. Schematic illustration of preparation of tri-component composite CFA@CS@TiO_2.

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Pego power plant (Portugal) for the fly ash samples.

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Degradación enzimática del antibiótico sulfametoxazol mediante lacasa *Trametes Versicolor* empleando siringaldehído como mediador redox

Manuel A. Figueredo[1,*], Ana M. Chavez[1], Inmaculada Rodríguez[1] y Pedro M. Álvarez[1]

[1]Departamento de Ingeniería Química y Química-Física, Facultad de Ciencias de la Universidad de Extremadura, Avda Elvas s/n, Badajoz, España

La excesiva presencia de residuos antibióticos en estaciones depuradoras de aguas residuales (EDAR) se ha convertido en un tema de gran preocupación actual por la proliferación de bacterias y genes con resistencia microbiana (ARB y ARG) [1]. Por ello, la eliminación de antibióticos en EDAR comienza a considerarse una prioridad en el tratamiento de aguas residuales. Los métodos convencionales de tratamiento arrojan, en general, pobres rendimientos en la degradación de antibióticos por lo que se están estudiando alternativas para complementar estos tratamientos convencionales. Entre ellas puede considerarse la degradación enzimática como un proceso catalítico selectivo y ambientalmente sostenible [2]. En este trabajo se ha empleado *Laccasa Trametes versicolor* (LAC) para la degradación del antibiótico sulfametoxazol (SMX). Las lacasas son enzimas de tipo oxidorreductasa que contienen cobre y pueden catalizar la oxidación de una amplia variedad de compuestos fenólicos y no fenólicos. No obstante, a pesar del potencial de oxidación-reducción de las lacasas, a veces la enzima no es capaz de oxidar por sí misma los sustratos siendo así necesaria la incorporación de mediadores redox. En este trabajo se ha estudiado el efecto de siringaldehído (SYR) como mediador natural.

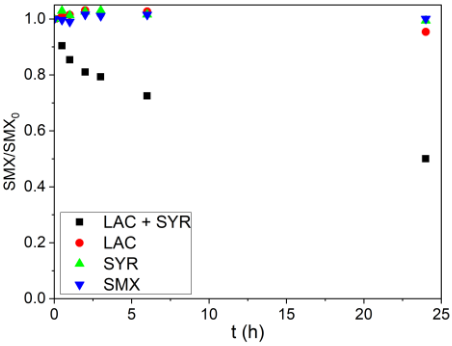

Fig. 3:Ensayos de eliminación de sulfametoxazol a pH 7,5 y 20 ºC. Condiciones iniciales: SMX=0,5 mg/L; SYR=0,05 mM; LAC=0,5 g/L

En primer lugar, se estudió la estabilidad de LAC en agua ultrapura y agua residual urbana. Mientras que en el primer caso la enzima mantenía su actividad durante tiempos prolongados de contacto (> 10 días), en agua residual se observó una pérdida drástica de actividad tras 6 días. Se comprobó que para lograr una degradación apreciable de SMX se requería la presencia del mediador redox, SYR, en concentración 0,01-0,05 mM (Fig. 1). Durante el tratamiento enzimático se produce cierto consumo de este mediador redox, por lo que se requiere un exceso del mismo. La eliminación de SMX fue más favorable en agua ultrapura que en agua residual, probablemente debido a un efecto de inhibición enzimática causada por componentes de la matriz residual.

Agradecimientos

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Carbocatalizadores híbridos GO-TiO$_2$ y G-GP-TiO$_2$ para reducción del potencial de formación de subproductos de desinfección mediante PAO basados en ozono

Jiménez-López, M.A.[*1], **Álvarez, P.M**[1]**., Beltrán F.J.**[1]

[1]Instituto Universitario de Investigación del Agua, Cambio Climático y Sostenibilidad (IACYS),
Universidad de Extremadura. Avda. de Elvas s/n. 06006 Badajoz, España
**e-mail: majimlopez@unex.es*

La utilización de cloro para eliminar microorganismos patógenos en el tratamiento de aguas es una técnica ampliamente extendida. Sin embargo, la utilización de este, trae implícita e inevitablemente la formación de subproductos de desinfección halogenados (DBPs) por la reacción del cloro con la materia orgánica natural (NOM) presente en el agua. Este hecho, es un problema bastante común en las estaciones de tratamiento de agua potable (ETAP). Recientes estudios afirman que estos compuestos podrían suponer un riesgo para la salud y cancerígenos [1].

Para intentar paliar este problema, se sintetizan materiales híbridos a base de dióxido de titanio y óxido de grafeno o grafeno ozonizado en fase gas para ser estudiados en Procesos Avanzados de Oxidación (PAO) basado en ozono y ozono-luz con el objeto de reducir el potencial de formación de trihalometanos (THM), ácidos haloacéticos (HAA) y el total de compuestos orgánicos halogenados (AOX) de un agua con ácido húmico (HA).

Los materiales utilizados fueron óxido de grafeno y grafeno comercial, este último ozonizado en fase gas para crear puntos nucleofílicos, y ambos sintetizados mediante un tratamiento de deposición en fase líquida con hexafluorotitanato de amonio para conseguir el material híbrido [2].

Tras la evaluación de los materiales en experimentos de ozonización fotocatalítica, todo apunta a que el material que mejores resultados arroja es el GO-TiO$_2$, el cual consigue una mayor eliminación de los parámetros estudiados.

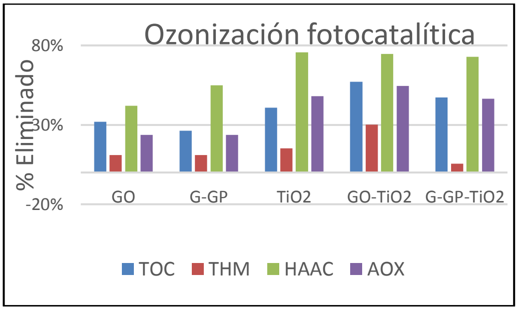

Fig.1. Porcentaje de eliminación de TOC, THM, HAA y AOX para los materiales estudiados.

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Shrimp shells waste as bioresource for antioxidant extracts and N-doped carbon materials

Inês S. Marques[1*], Flávia Gonçalves[1,2], Diana M. Fernandes[1], Manuela M. Moreira[2], Andreia F. Peixoto[1]

[1]REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
[2] REQUIMTE/LAQV, Instituto Superior de Engenharia do Inst. Politécnico do Porto, Porto, Portugal
**up201608306@fc.up.pt*

The current environmental and energy crisis has encouraged the industry to shift the production of chemicals from fossil resources to natural sources. So, the biorefinery concept is an essential strategy to convert biomass residues into value-added products and energy [1]. Global production and consumption of seafood is increasing, with shrimp shells contributing the most to this consumption and consequent waste (~6-8 million tonnes per year). Most shrimp shell waste (SSW) is landfilled, which leads to environmental and health problems. Therefore, the valorization of these scraps can bring environmental and economic benefits. Shrimp shell is made up of 3 main components: 20-50% calcium carbonate, 20-40% protein and 15-40% chitin [2,3]. In this project we aim to produce N-doped biochar-based catalysts for sustainable catalytic production of bioamines under new sustainable catalytic routes aiming to turning waste into wealth through innovative and potentially economical approaches. The N-doped biochar-based catalysts were prepared by wet-impregnation or ball-milling. In addition to evaluate the potential of the SSW extracts we used advanced extraction technologies including ultrasound assisted extraction and alternative solvents to obtain extracts rich in bioactive compounds, specially astaxanthin a lipophilic carotenoid belonging to xanthophyll family and a powerful antioxidant. Work is in progress in order to characterize the obtained extracts by different spectrophotometric assays, namely total phenolic and carotenoid content, as well as to determine their antioxidant activity by DPPH and ABTS assays.

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Feasibility of continuous flow photo-Fenton treatment using a magnetically separable Fe_3O_4/TiO_2 catalyst

André Torres-Pinto[1,2,*], **Julio J. Conde**[3,*], **C. Vázquez-Vázquez**[4], **Joaquim L. Faria**[1,2], **Cláudia G. Silva**[1,2], **Adrián M.T. Silva**[1,2], **Maria Teresa Moreira**[3]

[1] ALiCE – Associate Laboratory in Chemical Engineering, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
[2] Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
[3] CRETUS, Department of Chemical Engineering, Universidade de Santiago de Compostela,15782 Santiago de Compostela, Galicia, Spain
[4] Laboratory of Magnetism and Nanotechnology, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Galicia, Spain
**andretp@fe.up.pt*; *julio.conde@usc.es*

The classical Fenton process involves the combination of hydrogen peroxide (H_2O_2) and dissolved iron species (Fe^{2+}) to generate highly reactive hydroxyl radicals ($HO^{\bullet}$) for wastewater treatment. This advanced oxidation process (AOP) has evolved by implementing radiation (photo-Fenton) and/or magnetic heterogeneous catalysts that are easily separated from the treated wastewater. In particular, these magnetically recoverable catalysts opened the possibility of overcoming the main drawbacks of the classical homogeneous option, *i.e.*, massive sludge production and the need for acidic pH operating conditions.

Magnetite (Fe_3O_4) immobilised on a mesoporous silica matrix has presented high catalytic activity in the heterogeneous Fenton process for removing dyes and endocrine-disrupting compounds, with minimal catalyst losses in the separation step [1]. Moreover, high reaction rate constants were obtained with the same catalyst for the degradation of five pharmaceutical substances in photo-Fenton experiments [2]. Thus, in the next step, the nanostructured Fe_3O_4 material was combined with an optical semiconductor (TiO_2). The Fe_3O_4/TiO_2 catalyst has shown promising results in the degradation of micropollutants at the laboratory scale after optimisation of the catalyst composition, H_2O_2 concentration and operating pH, among other studied parameters. Moreover, this composite material achieved a high degradation of Orange II using visible-LED irradiation [3].

In the present work, the Fe_3O_4/TiO_2 nanoparticles were tested for the photo-Fenton degradation of the antidepressant venlafaxine (VFX, 200 μg L^{-1}) in water, using a laboratory-scale continuous flow reactor under visible-LED irradiation. VFX removals between 80 and 95% were achieved in 20 min.

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Comparative study on the correlation of pore sizes of different porous structures (MOF-808, UiO-66-NH_2, ZIF-8) on the catalytic performance of LnPOM-based composites in ODS studies

Simone C. Fernandes[1*], **Daniela Flores**[1], **Daniel Silva**[1], **Isabel Santos-Vieira**[2], **Carlos M. Granadeiro**[1], **Luís Cunha-Silva**[1], **Baltazar de Castro**[1], **Fátima Mirante**[1], **Salete S. Balula**[1]

[1]LAQV/REQUIMTE, Faculty of Sciences, University of Porto, 4169-007, Porto, Portugal
[2]CICECO - Aveiro Institute of Materials of University of Aveiro, 3810-193, Aveiro, Portugal
**up201603496@fc.up.pt*

The combustion of sulfur-based compounds, present in fuels results in the emission of hazardous gases, namely, sulfur oxides (SO_x). One of the many challenges for petroleum industries has been the treatment of fuels, for example, the removal of sulfur. Currently, strict legislation has been established demanding low sulfur limits for road fuels (S < 10 ppm).[1] Hydrodesulfurization (HDS) is the traditional method for the removal of sulfur in fuels. However, HDS is based on expensive technology. Therefore, effort has been put in to the development of alternative and/or complementary methods to the HDS, for example, oxidative desulfurization (ODS). Through ODS, sulfur refractory compounds can be removed from fuels using moderate temperature and atmospheric pressure. ODS occurs in two main steps: oxidation and extraction. The first step requires the activation of the oxidant, e.g., H_2O_2, by a catalyst.[2]

Polyoxometalates (POMs) have been widely studied as catalysts in ODS, including by our research group.[3] Recently, the study of lanthanopolyoxometalates (LnPOMs) as active centers for ODS has shown promising results.[4] The presence of lanthanides, through the coordination of lanthanide ions, i.e. Eu^{3+}, Tb^{3+}, Sm^{3+}, in the structure of POMs introduces interesting photoluminescence properties to the catalyst.[5] Nevertheless, POMs in general are highly soluble in catalytic media behaving as homogeneous catalysts, which complicates removal from media to reuse. Therefore, their heterogenization by immobilization in adequate solids supports, such as metal-organic frameworks (MOFs), provides the preparation of active heterogeneous catalysts with robustness and easy recovery from reaction. The effectiveness of POM@MOF catalysts has been shown in previous studies.[6]

In this work, we prepared three composites materials containing as active center the europium Lindqvist $[Eu(W_5O_{18})_2]^{9-}$ (abbreviated as EuW_{10}) encapsulated into three nanoporous support, MOF-808, UiO-66-NH_2 and ZIF-8. The composites were caracterized by various characterization techniques such as FT-IR, XRD, SEM/EDS and ICP-OES. The three composites EuW_{10}@MOF-808, EuW_{10}@UiO-66-NH_2 and EuW_{10}@ZIF-8 were studied as heterogeneous catalysts for the desulfurization of a multicomponent model fuel containing 1500 ppm of sulfur. Several reactional conditions were studied such as effect of the extraction solvent, quantity of active center and oxidant, which demonstrated that LnPOMs garantee very high catalytic performance with very low amounts of active centers. The recycling capacity and stability of the best performing catalyst was also investigated. The comparative study of the three heterogeneous catalysts revealed a correlation between the size of the active center and the sizes of windows and internal diameters of the support's pores.

Acknowledgements

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Photocatalytic oxidative coupling of amines by titanites perovskites

Joana C. Lopes[1,2,*], **Maria J. Sampaio**[1,2], **Cláudia G. Silva**[1,2], **Joaquim L. Faria**[1,2]

1. LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
2. ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

**joanacl@fe.up.pt*

Heterogeneous photocatalysis has appeared as a sustainable and promising technology for several applications: hydrogen production, carbon dioxide reduction, water treatment and organic synthesis. The main advantages of using semiconductor photocatalysis include operating under mild conditions (temperature and pressure) and the generation of non-toxic wastes. Moreover, the photocatalytic processes are activated by a light source, which enables the use of natural resources, such as solar light. Photocatalysis is an alternative for synthesising a varied range of organic compounds, namely imines. Due to its wide application in many fields, there has been an increased interest in recent years. Increasing attention has been focused on the direct synthesis of imines through the oxidative coupling of benzylamines, owing to reduced energy consumption and the application of a simplified process.

Several photocatalysts were already developed and exhibited high photocatalytic performance for chemical transformations, namely metal oxides (*e.g.*, titanium dioxide [1]), as well metal-free catalysts such as graphitic carbon nitride [2]. Perovskites are an exciting class of semiconductor materials with broad applications in solar cells. Due to their electronic properties, many perovskite materials have an excellent capacity as efficient photocatalysts under visible-light irradiation. Moreover, the perovskite crystal structure provides a good framework, which enables tuning the edge potentials to suit the needs of specific photocatalytic reactions.

In this work, $XTiO_3$ (X = Sr and Ca) perovskites were selected for the photocatalytic synthesis of imines by the oxidative self-coupling of amines. The $XTiO_3$ were synthesised by a simple hydrothermal method, yielding a crystalline material. Different techniques were used to characterise the catalysts. Diffuse reflectance UV-vis and photoluminescence were used to evaluate the optical properties of the materials. Scanning electron microscopy analyses were also performed to examine the morphological characteristics. Elemental analyses were carried out to determine the chemical composition of the synthesised materials. The photocatalytic performance of $SrTiO_3$ and $CaTiO_3$ was evaluated for converting benzylamine (BZA) into N-benzylidenebenzylamine (BZI) under aerobic conditions. After 6 hours of reaction under UV irradiation, 99 % and 92 % of BZA conversion was achieved with 66 % and 58 % of BZI selectivity using $SrTiO_3$ and $CaTiO_3$, respectively. To clarify the photocatalytic mechanism, the main active species in the reaction process were determined by quenching experiments.

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ENSEÑANZA DE LA QUÍMICA

Determinación de la dureza en las aguas. Ablandamiento de aguas por intercambio iónico

José María Fernández Solís*, **Elia Alonso Rodríguez, Victoria González Rodríguez, Elena González Soto, Jesús Manuel Castro Romero**

Departamento de Química, Área de Química Analítica, Escuela Politécnica de Ingeniería de Ferrol (EPIF),
Universidade da Coruña (UDC), 15403 Ferrol, España
**jose.maria.fsolis@udc.es*

En los planes de estudios de los Grados en Ingeniería Eléctrica y en Ingeniería Electrónica Industrial y Automática de la Escuela Universitaria Politécnica de Ferrol (Universidad de A Coruña), se incluye la asignatura de carácter obligatorio: Ingeniería Ambiental, en cuyo programa figura el tema 2 "Contaminación de las aguas" [1]. En dicho tema se tratan los subtemas: parámetros de calidad de las aguas y parámetros generales indicadores de la contaminación. En dicha asignatura se realizan 5 prácticas de laboratorio, de las que 4 están relacionadas con los subtemas citados. Una de ellas se titula dureza y ablandamiento de aguas. Originalmente se entendió por dureza del agua, la medida de su capacidad para precipitar el jabón. Se debe a la presencia de iones calcio y magnesio en disolución, aunque también contribuyen a ella otros cationes divalentes como los de estroncio, hierro y manganeso. Los aniones asociados con estos cationes son los bicarbonatos, sulfatos, cloruros y nitratos. La dureza se expresa por la cantidad equivalente de carbonato de calcio en mg/L [2].

Es bien conocida la existencia de métodos volumétricos de determinación de la dureza en aguas empleando disolución patrón de AEDT y negro de eriocromo T o calmagita como indicador [3]. En la presente comunicación se describe un procedimiento rápido, sencillo y económico para la determinación de la dureza en aguas, usando licor hidrotimétrico (LH) y una bureta hidrotimétrica (método de Boutron y Boudet) [4], y un segundo método de ablandamiento de aguas.

Inicialmente, se toma una parte alícuota de la muestra de agua problema y se lleva a un frasco de vidrio graduado; si se sospecha una dureza elevada, se diluye al volumen final con agua destilada. Se llena y enrasa la bureta con licor hidrotimétrico, se adiciona al agua contenida en el frasco, se tapa y agita fuertemente. Si se forma espuma y persiste como mínimo 2 minutos, la valoración se da por terminada, obteniéndose la dureza en grados hidrotimétricos. En una segunda experiencia, se hace pasar otra parte alícuota de la muestra a través de una columna rellena con resina de intercambio catiónico; se determina la dureza del agua eluida a través de la resina y se comparan los resultados de las dos experiencias [4,5]. Finalizado el procedimiento experimental y los cálculos, con el fin de verificar si el alumno ha comprendido y asimilado los conocimientos expuestos, éste resolverá unas cuestiones sencillas, relacionadas con el desarrollo de la práctica y con su fundamento teórico.

Finalmente se hace hincapié en las aplicaciones de las resinas de intercambio iónico en Química Analítica: a) en separaciones analíticas (eliminación de iones interferentes, iones con propiedades analíticas semejantes, concentración de iones en disoluciones diluidas, preparación de disoluciones patrón, separación y concentración de electrólitos) [6,7]; b) en separaciones por cromatografía iónica.

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Práctica virtual de Laboratorio de Química: Determinación del calor de combustión y de formación de la aspirina (ácido acetilsalicílico)

J. M. Fernández Solís[1,*], A. M. Gómez Rodríguez[2], M. J. Rodríguez Guerreiro[1], S. Fernández Alonso[2]

Departamento[1] y Laboratorio[2] de Química, Escola Politécnica de Enxeñaría de Ferrol (EPEF),
Universidad de A Coruña (UDC), Mendizábal s/n, 15403, Ferrol, España
jose.maria.fsolis@udc.es

Nuestra experiencia como docentes nos indica que, debido a la progresiva disminución de las horas asignadas a la asignatura Química en los planes de estudios antiguos y en los de los actuales Grados de Ingeniería, el tiempo que el profesorado dedica a las prácticas de laboratorio es pequeño, reduciéndose la presencia física del alumnado en el laboratorio a un valor casi testimonial. En consecuencia, la presentación de videos con carácter descriptivo sobre prácticas virtuales en el aula, sin los inconvenientes debidos a la falta de espacio en el laboratorio, permite al profesor poder impartir detalladamente la práctica que corresponda, promoviendo e impulsando el debate con los estudiantes y favoreciendo una mejor comprensión de los conceptos explicados.

Las consideraciones anteriormente expuestas nos han conducido a llevar a cabo un estudio sobre prácticas virtuales de Química que pudiesen complementar a las realizadas en el laboratorio, sin pretender nunca que llegasen a sustituirlas, ya que se considera imprescindible que el estudiante adquiera las competencias relacionadas con el trabajo experimental a desarrollar en el laboratorio.

Con ese fin se realizaron prácticas, en las áreas de la Química General y Analítica, relativas a preparación de disoluciones [1,2,3], calor de reacción [2,3], valoraciones ácido-base [1], identificación de iones a partir de sus mezclas en disolución [4] y de metales a la llama, determinación de propiedades termodinámicas [5], usando el programa virtual ChemLab, General Chemistry Laboratories, v.2.5, anexo al texto de Pearson Educación [6].

Esta comunicación describe una práctica con objeto de determinar el calor de combustión de la aspirina, mediante los datos obtenidos en un experimento efectuado en un laboratorio virtual de Química. A partir del valor obtenido, se determina, por aplicación de la ley de Hess [7], el calor de formación de dicha sustancia. El programa informático usado permite la elaboración de un video, a visualizar por los estudiantes, en el que se describen las etapas del experimento, debiendo anotar los valores de los parámetros necesarios para el cálculo de dichos calores de combustión y de formación, obteniendo resultados concordantes con los valores considerados de referencia [8,9]. Finalizada la práctica, y para verificar la comprensión y asimilación de los conocimientos expuestos, el profesor propondrá a los alumnos la resolución de unas cuestiones sencillas en relación con dicha práctica.

Agradecimientos

Queremos expresar nuestro agradecimiento a la Universidad de A Coruña, por la concesión de una Beca de Colaboración en Laboratorios de Docencia a Andrea Gómez Rodríguez, y a la Editorial Pearson Educación.

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Caso Práctico: evaluación de la corrosión en armaduras de hormigón por medio de la medición del campo potencial

Santiago Urréjola-Madriñán[1,*], Rosa Devesa Rey[1], Miguel Ruiz Ruiz[1], Lorena González-Gil[1]

[1]Centro Universitario de la Defensa, Escuela Naval Militar, Plaza de España, s/n, 36920, Marín (Pontevedra), España
urrejola@cud.uvigo.es

En las asignaturas que estudian el comportamiento frente a la corrosión de diversos materiales, es enriquecedor que, además de estudiar a nivel de laboratorio estos problemas, proponer a los alumnos diversos trabajos con equipos industriales. En el presente trabajo se propuso al estudiante la evaluación de la corrosión del hormigón armado expuesto a un medio marino utilizado un método clásico de análisis de determinación de pesos [1], comparándolo con un método electro químico, como es el análisis del campo potencial, usando el equipo comercial Canin+®, mostrado en la figura 1.

En las armaduras de hormigón se produce una capa pasiva de óxido de hierro hidratado que las protege de la corrosión. Al degradarse esta capa pasiva aparecen zonas anódicas y catódicas (Fe^{2+}, OH^-) creándose una diferencia de potencial que se puede medir con equipos especializados [2]. La exposición de las probetas al medio marino se lleva a cabo en el laboratorio mediante una solución de NaCl al 3,5% y agua. La evaluación se realiza empleando un sistema de análisis de campo potencia mediante el analizador Canin+®. Las probetas utilizadas disponen de tres barras de acero corrugado con un diámetro de 10 mm y calidad B 500 SD (UNE 36068:2011), se toman medidas siguiendo las instrucciones del equipo. Figura 2.

Dado que el proceso de corrosión necesita un tiempo superior al que se dispone en prácticas, los valores de pérdida de peso se le dan al alumno, que simplemente los trata y compara con los resultados de las medidas de campo potencial que obtiene con el Canin+. Para la toma de datos se colocan dos electrodos, uno de los electrodos de referencia sobre la superficie del hormigón y otro entre el acero de las armaduras, de esta manera se puede determinar la diferencia de potencial eléctrico existen. Los valores obtenidos nos proporcionan un valor del potencial de corrosión, E_{corr}, que nos permite obtener valores orientativos del grado de corrosión, de manera que tendrá una validez estrictamente cualitativa, tal y como se muestran en la tabla 1. Los mapas de campo potencial y frecuencia acumulada de potencial obtenidos tendrán la forma que aparece en la figura 3.

Durante el desarrollo del trabajo el alumno verifica el correcto funcionamiento del método de evaluación de la corrosión empleando potenciales de circuito abierto, para medir el potencial de corrosión, comparando los resultados con los datos de la variación de pesos de las probetas.

Tabla 1. Valores de E_{corr} y riesgo de corrosión [3]

E_{corr} (SCE) (mV)[a]	Riesgo corrosión
> -200	10 %
-200 a -300	50 %
< -350	90 %

[a] Potencial de corrosión frente al electrodo de calomelanos saturado (SCE)

Fig.1. Equipo comercial Canin+®

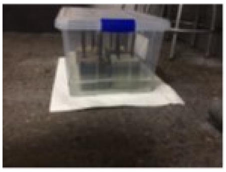

Fig.2. Probetas en exceso de agua salada

Fig.3. Ejemplo de mapa de potencial, izquierda, y frecuencia acumulada, derecha.

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QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Synthesis of activated carbons from food and wood industrial by-products and application for dyes removal

<u>C. H. Pimentel</u>*, A. Ferreiro-Salgado, M.S. Freire, D. Gómez-Díaz, J. González-Álvarez

Departament of Chemical Engineering, School of Engineering, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, Spain
**catarinahelena.dasilveira@rai.usc.es*

In recent decades, a serious threat to the environmental system is water pollution, thus, reducing pollutants from wastewater before discharging to the environment is required. Dyes are extensively used in industry and are the first identified contaminants in industrial wastewaters. Moreover, the majority present high toxicity and their stability against light and oxidants makes their degradation difficult [1, 2]. Several techniques have been used to remove dyes from aqueous solutions and adsorption has been highlighted due to its various advantages [1]. Carbon materials are highly attracting adsorbents and their effectiveness in pollutants removal has been found superior to other materials, due to their outstanding properties such as high specific surface area, porosity and superior surface reactivity. Despite that, its preparation continues to be expensive [2, 3].

In this regard, many efforts have been made to produce activated carbons (AC) from biomass residues since they are renewable, cheap and available in large quantities. In the present work, AC were produced from two wastes from the food industry, olive stones (O) and almond shells (A), and one from the wood industry, pine sawdust (P). For each precursor a material carbonized at 600ºC (PC, OC and AC) and two activated carbons prepared using potassium hydroxide at 850ºC and different carbon/activating agent ratios 1:4 w/w (PCA4, OCA4 and ACA4) and 1:2 w/w (PCA2, OCA2 and ACA2) were synthetized.

The carbons were characterized through different techniques such as point of zero charge (pH_{PZC}) determination and scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX). The carbon specific surface area was also determined by the Brunauer-Emmett-Teller (BET) equation through N_2 and CO_2 adsorption isotherms.

The highest surface area measured with N_2 gas sorption for all materials was obtained at a carbon/sodium hydroxide ratio of 1:4 (Fig. 1) and the highest surface area and pore volume corresponded to PCA4, 2887.3 m^2/g and 1.6 cm^3/g, respectively. In addition, the behavior of carbons for dyes adsorption was investigated, and PCA4 and OCA4 could effectively adsorb a blue wood dye from aqueous solutions with removal efficiencies of 99.8% and 97.5%, respectively, at an initial dye concentration of 500 mg/L and an adsorbent dose of 0.5 g/L, which demonstrates their potential for the treatment of colored effluents.

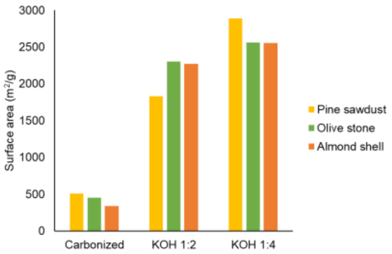

Fig.1. Specific surface area determined with N_2 adsorption-desorption isotherms.

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Removal of the inert coating from waste printed circuit boards using NaOH solutions under autoclaving treatment

V. Rahimi[1,*] , **D. Gómez-Díaz**[1], **M.S. Freire**[1], **J. Gónzalez-Alvarez**[1]

[1] Department of Chemical Engineering, School of Engineering, Universidade de Santiago de Compostela Rúa Lope Gómez de Marzoa s/n. 15782, Santiago de Compostela, Spain

[*] *vahid.rahimi@rai.usc.es*

Electronic waste (e-waste) refers to all sorts of electronic equipment and devices which are discarded and reached the end of their useful life [1]. Printed circuit boards (PCBs) are essential part of almost all the electronic products [2] and, account for an estimated 3-5 wt.% of the e-wastes [3]. Moreover, waste PCBs could be a rich secondary source of base and precious metals, therefore, their recycling is beneficial not only for the recovery of valuable resources but also to protect the environment [4]. Metals present in the PCBs are covered by a chemical coating, which is commonly made of epoxy. In a hydrometallurgical process, this coating does not allow the leaching agent to penetrate through it and prevents its contact with the metals. On the other hand, to process the PCBs in an environmentally friendly manner, toxicity can be reduced by removing the epoxy coating from the PCBs.

To eliminate the coating using conventional methods, a 10M (40%) sodium hydroxide solution is usually employed as removing agent at room temperature [5, 6], but it is a waste of time and reagents. In this study, an alternative stripping method using less concentrated NaOH solutions under autoclaving conditions was used. Thus, PCBs samples were put in contact with sodium hydroxide solutions at different concentrations (1% and 10%) and a solid/liquid ratio of 200 g/L and then were kept in an autoclave at a 121° C and 1.1 bar for 1 h.

The results indicated that the epoxy coating on the PCBs was completely eliminated with both NaOH concentrations in one hour. For the highest NaOH concentration, the coating layer got peeled like a sheet remaining some parts strongly adhered to the PCBs, whereas for the lowest concentration the sodium hydroxide broke the coating in small particles. In this way, the disintegrated coating was dispersed in the solution. Hence, the PCBs treated with 1% NaOH solution required less physical energy for posterior brushing in comparison with those treated with the high concentration (10%). Subsequently, the concentration of dissolved metals in both NaOH solutions was determined using ICP-OES finding that metal loss was much lower using the low NaOH concentration than the high one (Figure 1). As the main objective of these experiments was to achieve a great efficiency in removing the PCBs coating minimizing metal losses but optimizing the consumption of time and reagents and, moreover, reducing the environmental and human health risks of the process, removing with a 1% NaOH solution under autoclaving conditions was selected to continue experimentation.

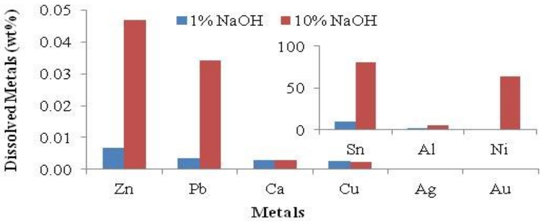

Fig.1. Metals dissolved in NaOH solutions

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EFFECT OF DIALYSIS AND PURIFICATION ON BIOACTIVITY OF *ASCOPHYLLUM NODOSUM* SEAWEEDS EXTRACTS

Mauro Gisbert, Ramón Moreira, Jorge Sineiro*

Chemical Engineering Department, ETSE, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15780 Santiago de Compostela, Spain
**jorge.sineiro@usc.es*

Isolation and chemical characterization of phlorotannins has gained special attention due to their array of health-promoting benefits. Antioxidant capacities of phlorotannins are related to their structure and molecular size (i.e., degree of polymerization), so scavenging activity increased with increasing polymerization. Separation technologies are widely applied for the purification and isolation of their highest bioactive fractions. However, molecule with different sizes often show similar chemical properties, making their isolation hard. It is proposed the study of bioactivity and physico-chemical features of diverse molecular size fractions of phlorotannins extracted from *Ascophyllum nodosum* (AN) seaweeds. AN was soaked for 15 min at 170 rpm and room temperature (rt) with distilled water at liquid-solid ratio of 20 g/g, Fig A. Then, mixture was sonicated at 90 W/cm^2 for 2 min to obtain crude extract (EW) that was further purified (PW). Finally, PW was dialyzed with molecular weight cut-off dialysis cassettes of 20 (PD20), 10 (PD10), 3.5 (PD3) and 2 kDa (PD2). The cassettes were clamped and immersed in a reservoir of distilled water and shaken (120 rpm) at 4 ºC for 120h (Fig B). The content of polyphenol (TPC), and antioxidant activity (DPPH) together with nuclear magnetic resonance (^{1}H-NMR) and quadrupole time-of-flight mass spectrometry (Q-Tof-MS) provided proximate chemical composition, average molecular size and antioxidant activity (Fig C and D). Dialysis showed that main bioactive fraction of phlorotannins was found at 20 kDa or higher molecular sizes (Fig C) showing that higher size phlorotannins provided the main antioxidant activity in seaweed extracts [1]. Besides, proposed analysis allowed to follow the reduction in phlorotannin content with purification and dialysis treatments. Nevertheless, dialysis and purification treatments evidenced that some fractionation treatments may not always be a good option to increase bioactivities of seaweeds derived products [2]. The development of a food-friendly process for the extraction and enrichment of phlorotannins from macroalgae is vital to facilitate their use in new generation functional foods.

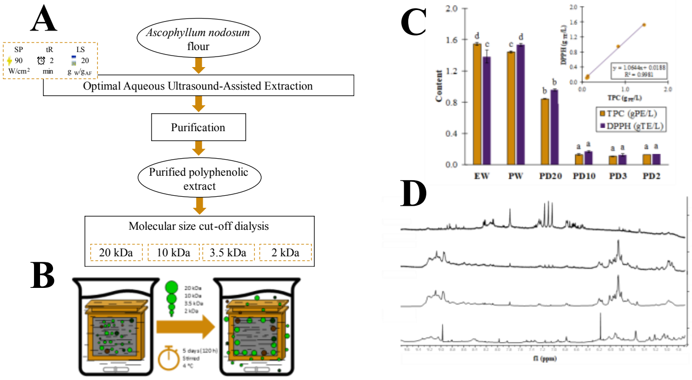

Figure. Process scheme (A), dialysis proposed system (B), bioactivities (C) and NMR (D) of samples.

Agradecimientos

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Sugars and short-chain oligogalacturonides productionfrom lemon peels

S. Martínez-Gómez[1,2], David González-Formoso[1], B. Míguez.[1,2], S. Rivas[1], R. Yáñez[2,3], J.L. Alonso[1,2]

[1]Universidade de Vigo, Facultade de Ciencias, As Lagoas s/n, 32004 Ourense, Spain
[2]CINBIO, Universidade de Vigo, 36310 Vigo, Spain
[3]Universidade de Vigo, Escola de Enx. Industrial, Campus Lagoas-Marcosende, 36310 Vigo, Spain
*xluis@uvigo.es

The human gut microbiota is an abundant and diverse ecosystem which plays an important role in human health and it can be positively influenced by the intake of prebiotics. The ISAPP defined a prebiotic as “a substrate that is selectively utilized by host microorganisms conferring a health benefit” [1].

In recent years, important efforts have been made in the development of new prebiotics with, potentially, improved and additional properties. In this context, low-DP oligogalacturonides (OGalA) showed very interesting biological properties [2, 3].

The juice industry generates huge amounts of lemon peel wastes (LPW) every year. LPW are rich in free sugars and pectin, a polymer whose backbone is mainly made of galacturonic acid units.

The aim of this work was to develop an environmental friendly process for the production of hexoses-rich solutions and low-DP oligogalacturonides (OGalA) mixtures using LPW as a raw material.

For achieving this objective, LPW samples were subjected to a three-step aqueous extraction at room temperature in order to recovery free sugars. Then, the resulting solids were treated by hydrothermal treatment under non-isothermal conditions (up to Tmax=155ºC) and the autohydrolysis liquors were recovered by filtration and partially hydrolysed with commercial pectinases in order to reduce the average DP of oligomers.

Solutions containing up to 17 g sugars/L (mainly glucose and fructose) were obtained during the first extraction step, whereas the autohydrolysis treatment resulted in liquid fractions enriched in OGalA (>50%), with low impurities contents (close to 12.5%). Finally, the enzymatic hydrolysis of these liquors using polygalacturonases, yielded mixtures of oligosaccharides with an estimated average DP from 4.5 to 2.9, without monomers generation.

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EFFECT OF METHOD, SOLVENT AND LIQUID–SOLID RATIO ON PHLOROTANNINS EXTRACTION FROM *ASCOPHYLLUM NODOSUM* SEAWEEDS

Mauro Gisbert, Jorge Sineiro, Ramón Moreira*

Chemical Engineering Department, ETSE, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15780 Santiago de Compostela, Spain

**ramon.moreira@usc.es*

Phlorotannins extraction is often carried out using organo-solvents that are volatile, inflammable, and toxic. However, water, as an efficient and green-label solvent, is proposed for polyphenols extraction from *Ascophyllum nodosum* brown seaweed (AF). Two different extraction methods, conventional solid-liquid extraction (SLE) and ultrasound–assisted extraction (UAE) were studied, at several liquid-solid ratios for both methods (20 to 40 $g_{solvent}/g_{seaweed}$). Saltwater solvent (S) (3.6 g/L NaCl content) and distilled water (D) were studied to replace organo-solvents.

For SLE, AF was soaked for 60 min at 170 rpm and room temperature (rt) with D- and S- solvent. SLE kinetics employing both solvents (D and S) were successfully modelled by Peleg's model from 2 to 60 min. For UAE, AF was mixed with solvents (D- and S-) and sonicated at 90 W/cm^2 for 15 min (Figure 1).

Aqueous SLE and UAE extracts were chemically characterized by means of polyphenol content (TPC) and antioxidant activity (DPPH) for both D- and S-solvents to determine the extraction kinetics (Figure 2A), equilibrium times, extraction yields (Figure 2B).

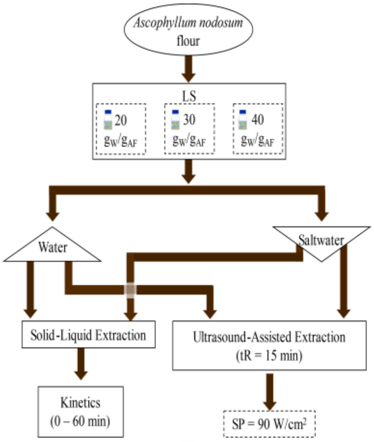

Figure 1. Process

TPC and DPPH values evidenced that, with similar times (15 min) UAE increased extraction yields. Similarly, lower LS values favored extractions and, finally, it was observed that D-solvent slightly increased extraction concerning with S-solvent.

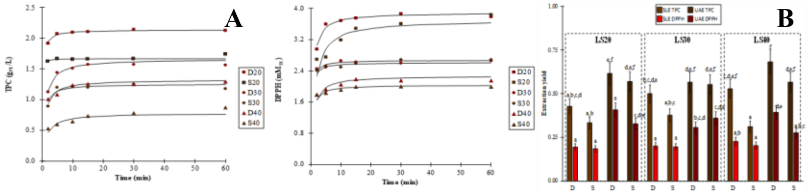

Figure 2. TPC and DPPH kinetics (A) and their extraction yields (B)

Results demonstrated that saltwater can be employed as eco-friendly solvent according to the green chemistry principles and sonication increased phytochemical compound extractions. The development of a food-friendly process for the extraction and enrichment of phlorotannins from macroalgae is vital to facilitate the use of this valuable resource in future developments of macroalgal-based functional foods.

Agradecimientos

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Sequential production of oligogalacturonides and arabinooligosaccharides by autohydrolysis of sugar beet pulp

S. Martínez-Gómez[1,2], B. Míguez[1,2], S. Rivas[1], R. Yáñez[2,3], J.L. Alonso[1,2]

[1]Universidade de Vigo, Facultade de Ciencias, As Lagoas s/n, 32004 Ourense, Spain
[2]CINBIO, Universidade de Vigo, 36310 Vigo, Spain
[3]Universidade de Vigo, Escola de Enxeñaría Industrial, Campus Lagoas-Marcosende, 36310 Vigo, Spain
**xluis@uvigo.es*

The colonic microbiota plays a crucial role in the human health, and it can be modulated throughout the diet and the intake of prebiotics. Although there is a variety of commercial prebiotics (as inulin or fructooligosaccharides), there is also an increased interest on the production, evaluation and commercialization of new ones with, potentially, improved and additional properties. In this context, pectin-derived oligosacharides (denoted POS) are a promising alternative.

Sugar beet pulp (SBP) is a pectin-rich byproduct generated in the sugar manufacturing plants that can be used as raw material for the production of POS. However, when SBP is processed by autohydrolysis, complex mixtures of oligomers (including oligogalacturonides, arabinooligosaccharides, galactooligosaccharides, etc.) are generated [1]. On the other hand, it is well known that the beneficial effects and further applications of a given carbohydrate depends on its physico-chemical properties (sugar composition, molecular weight, etc.). Therefore, to advance in the knowledge of the structure-function interrelationships, it is necessary to obtain isolated and well characterized products.

The aim of this work was to develop a novel process (based on a two-step hydrothermal treatment) for the separated production of liquid fractions enriched in oligogalacturonides and arabinooligosaccharides from sugar beet pulp.

For achieving this objective, samples of sugar beet pulp were subjected to a two sequential hydrothermal treatments under non-isothermal conditions up to temperatures in the range 130-140 ºC (first stage) and 160-175 ºC (second stage). At the end of treatments, liquors and solid fractions were separated by filtration and analysed according to the methods previously employed in this field [1].

Under selected conditions, mixtures rich in oligogalacturonides (>30%) or arabinooligosaccharides (>37%) were obtained after the first and second stage of hydrothermal treatment, respectively.

Acknowledgements

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How the addition of polyphenols from *Ascophyllum nodosum* seaweeds affects to corn starch gels rheology

L. Montes[1], M. Santamaria[2], R. Garzon[2], C.M. Rosell[2], R. Moreira[1*]

[1]Chemical Engineering Department, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15780 Santiago de Compostela, Spain
[2]Institute of Agrochemistry and Food Technology (IATA-CSIC). C/Agustin Escardino 7, 46980 Paterna, Spain
**ramon.moreira@usc.es*

Gluten-free products are in high demand as more people are diagnosed as having celiac disease. A gluten-free diet can promote a high glycemic index, therefore, a high relationship between type 1 diabetes and celiac disease exists [1]. Commonly, to improve the gluten-free products hydrocolloids are used but the aim of this work is improving the gluten-free products with polyphenols (PP) from *Ascophyllum nodosum* seaweeds which have many health benefits due to their antioxidant power offering protection against development diabetes [2].

Corn starch (CS) gels were made at two starch concentrations (1.95 and 5.0% w/w). For 1.95 % w/w samples, the PP/CS ratios were: 0, 0.5, 2.5 and 5.0; while for gels at 5.0% w/w the ratios were: 0, 0.2, 0.9 and 1.9, adding different amounts of PP solutions of 0, 0.1, 0.5 and 1.0 g/L. The rheological characterization was performed with stress-controlled rheometer (Anton Paar 301) with plate-plate geometry (50 mm) and a gap of 0.25 mm. All the samples were covered with light paraffin oil to prevent water evaporation. First, a pre-shear (100 s^{-1} and 75 min) was made for the adsorption of PP in starch. Then, a heating ramp from 25 to 90ºC (at 5°C/min) was carried out followed by a time sweep at 90ºC (30 min), a cooling ramp from 90 to 25ºC (at 3°C/min) and a time sweep at 25ºC (30 min) at a constant strain of 10% and a frequency of 1 Hz (inside LVR). Finally, a frequency sweep from 0.01 to 10 Hz was made at 10% of strain and 25ºC. Temperature was controlled by a Peltier system

Above gelatinization temperature (ranged between 70 and 73ºC) the gel was formed characterized by elastic modulus greater than the viscous modulus (G´ > G´´) for all samples. In the heating ramp the addition of PP enhanced the elastic character of the samples (higher G´) independently of starch content. During the time sweep at high temperature (90 ºC) the behavior was like the previous step, the PP addition increased G´ values. However, in the cooling profile, it was observed how the G´ values of the samples with PP have lower G´ values, indicating that the presence of PP delays the rapid retrogradation of the starch gel [3]. This behavior was observed for all samples except those corresponding to the lowest PP/CS at high starch content (5% w/w).

During the maturation step at low temperature (25 ºC) the previous behavior was enhanced. Finally, the frequency sweep showed a clear drop in G´ values of low starch content gels (1.95% w/w) from 39.6 to 26.7 Pa (at 1 Hz) with increasing PP/CS (from 0 to 5). However, for starch gels at 5% w/w, a different behavior was observed. Only at high ratio PP/CS (1.9) the G´ drop was observed, while gels with low PP/CS (< 0.9) no significant differences (in G´ and in damping factor G´´/G´) with control were found. These results indicated that the rheological behavior of starch gels was modified only when a threshold PP/CS ratio was achieved, and its value increased with increasing the starch content of gel (or strength).

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Adsorption of polyphenols extracted from *Ascophyllum nodosum* seaweeds on native corn starch and corn starch gel

L. Montes, R. Moreira*

Chemical Engineering Department, ETSE, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15780 Santiago de Compostela, Spain
**ramon.moreira@usc.es*

Ascophyllum nodosum is a brown seaweed with one of the highest content of a specific type of polyphenols called phlorotannins. Polyphenols are secondary metabolites and have many health benefits due to their antioxidant power offering protection against development of cancers, cardiovascular diseases, osteoporosis, and diabetes between others [1]. The objective of current work is to study the adsorption of polyphenols (PP) extracted from seaweed to corn starch (CS) and corn starch gel to evaluate their interactions in starchy food formulations.

The extraction of polyphenols from *Ascophyllum nodosum* was made with water as solvent employing a liquid/solid ratio of 20 during 15 min at room temperature (rt) under constant stirring (700 rpm). Then, the mixture was centrifuged, and the liquid phase was filtered. Total polyphenol content (TPC) of extract (2.74 ± 0.05 g/L) was determined [2]. Then, several dilutions were performed to obtain different polyphenols concentrations (0.1, 0.3, 0.5, 1.0, and 2.0 g/L). At these solutions, native or gelled corn starch was added at constant ratio (1.95% w/v). Corn starch gels were previously performed after heating starch solutions at 95 ºC during 20 min and cooling at room temperature during 45 min.

Polyphenols adsorption isotherms were carried out during 3 h until the equilibrium point is reached in an incubator (New Brunswick, Innova 40, USA) at 25 ºC and 200 rpm. TPCs of aqueous solutions were determined when equilibrium was achieved (no TPC changes between measures elapsed 20 min). Adsorbed polyphenols were evaluated by the corresponding mass balance. Figure 1 shows the equilibrium data, by the plotting of the final polyphenols concentration (g/L) of solution in front of the adsorbed polyphenols in the solid starch, q (g/g). Fig. 1a shows the adsorption curve for native corn starch. A maximum q value (around 0.12 g/g) was obtained at high polyphenols content (> 0.6 g/L) and the shape of the curve corresponded to a Langmuir isotherm (polyphenols adsorption on the starch surface is physically limited). A linear relationship was achieved between equilibrium concentration of liquid and starch gel of starch corresponding to Henry`s isotherm, Fig. 1b. Additionally, the polyphenols adsorption was notoriously enhanced using the starch gel against native starch achieving q values of 0.07 g/g. These results show that gel state increases the available surface area and interactions between starch polymers (amylose-amylopectin) with polyphenols are also promoted [3].

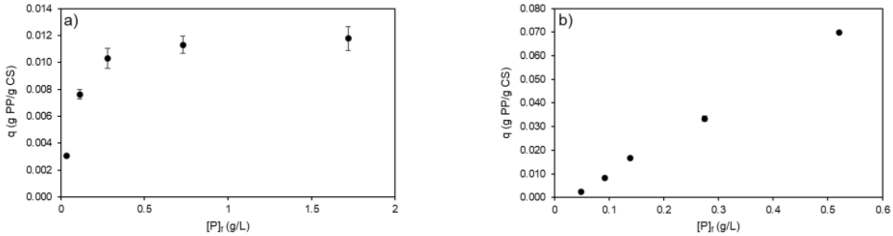

Fig.1. Adsorption of polyphenols of corn starch (a) and corn starch gels (b) at 25ºC.

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Eucalyptus globulus wood fractionation by organosolv processing

M. Fernández-Bautista[1,2], S. Rivas[1,2], C. Vila[1,2], V. Santos[1,2], J.L. Alonso[1,2], R. Yañez[2,3]

[1]Universidade de Vigo, Facultade de Ciencias, As Lagoas s/n, 32004 Ourense, Spain
[2]CINBIO, Universidade de Vigo, 36310 Vigo, Spain
[3]Universidade de Vigo, Escola de Enx. Industrial, Campus Lagoas-Marcosende, 36310 Vigo, Spain
**reme@uvigo.es*

Circular bioeconomy has been defined as the economic model that allows the use of different renewable biological resources and its conversion to various high-value bio-based products such as biofuels, biochemicals, bioenergy and others. Biomass, in particular lignocellulose, is a renewable feedstock that offers several benefits: carbon dioxide capture, low price and high availability [1]. An integrated biorefinery is a facility wherein various conversion technologies are integrated to efficiently maximize the biomass utilization. In this context, *Eucalyptus globulus* have several properties that make it a profitable lignocellulosic biomass source: high growth rate, low water consumption and high content of the target constituents (cellulose, lignin or hemicellulose). Furthermore, eucalypt stands for the 20.3% of all Galician forest and the 26% of all Portuguese forest surface [2].

On the other hand, organosolv pre-treatment is a fractionation technique that utilizes organic solvents or aqueous-organic mixtures at high temperatures, with or without the addition of catalysts, to recover cellulose as a solid stream and the hemicellulose and lignin-derived products in the liquid fraction [3].

In this work, a mixture of 1-pentanol/water (two almost immisicible solvents) was used for treating eucalypt wood, allowing obtain three separate streams in a single step process: hemicelluloses-derived products in the aqueous phase, lignin fragments in the organic one and cellulose in the solid stream [3, 4].

Eucalyptus globulus wood samples were subjected to organosolv processing using mixtures of 1-pentanol/water. Experiments were performed in a 100 mL Parr reactor at different temperatures, organic solvent content in liquid phase and catalyst concentrations, keeping constant the liquid to solid ratio and the reaction time. After cooling, the mixture was filtered to recover the solid phase, and aqueous and, then, the organic liquid phases were separated by decantation. Both, raw material and treated solids were characterized following the NREL standardized method [5], and the aqueous phase analysed for their content of oligosaccharides and monosaccharides as in previous works [4].

Under selected conditions (60% of organic solvent, 160 °C and 1% of catalyst), an efficient wood fractionation was achieved, including 84% of delignification, negligible glucan losses and almost complete solubilisation of hemicelluloses. Solutions containing up to 34g/L of xylose in monomeric and oligomeric form) were simultaneously obtained during the process.

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One-pot fractionation of *Pinus pinaster* wood by biphasic delignification with butanol/water

C. Vila[1,2], M. Fernández-Bautista[1,2], S. Rivas[1,2], V. Santos[1,2], J.L. Alonso[1,2], R. Yañez[2,3]

[1]Universidade de Vigo, Facultade de Ciencias, As Lagoas s/n, 32004 Ourense, Spain
[2]CINBIO, Universidade de Vigo, 36310 Vigo, Spain
[3]Universidade de Vigo, Escola de Enx. Industrial, Campus Lagoas-Marcosende, 36310 Vigo, Spain
**reme@uvigo.es*

The widespread issues caused by oil consumption and global industrialization are driving the search for an alternative to energy and materials production capable of replacing or mitigating our current dependence on oil. In this context, lignocellulosic materials are the most viable alternative due to their abundance and availability, high replacement rate, low cost, renewability and non-competitiveness with food applications (1).

The integral valorization of lignocellulosic materials (LMC), through the biorefinery approach, involves strategies for the recovery of each of their main components: cellulose, hemicelluloses and lignin (2). With this purpose, two-stage processes have been previously investigated: i) autohydrolysis for the selective solubilization of hemicelluloses, and ii) organosolv treatments for the production of solids and liquid phases enriched in cellulose and lignin, respectively.

However, in recent years, novel single stage treatments in biphasic systems have also been reported; since they allowed the simultaneous recovery of a solid fraction composed mainly of cellulose as well as two liquid phases, one organic and one aqueous, containing the solubilized lignin and hemicelluloses fragments, respectively (3).

This work deals with the treatment of *Pinus pinaster* wood in one single stage using a biphasic media of water/butanol acidified with sulfuric acid. Several experiments were carried out in a Parr reactor at 190 ºC and reaction times in the range 10-30 min, using an aqueous solution of 40% butanol (w/w) containing sulfuric acid (1%) as catalyst. Under selected conditions, treatments lead to cellulose recovery of 75%, as well as percentages of solubilization of hemicelluloses and lignin of 60% and over 70%, respectively.

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Concentration and purification of pectin extracts from sugar beet pulp using different ultrafiltration/diafiltration configurations

Fernández-Delgado M.[1,2*], **García-Cubero M.T.**[1,2], **Coca M.**[1,2], **Lucas S.**[1,2]

[1]Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain
[2]Institute of Sustainable Processes, Dr. Mergelina s/n, 47011 Valladolid, Spain
**marina.fernandez.delgado@uva.es*

Pectin is a natural fiber composed of different heteropolysaccharides, principally of D-galacturonic acid (GalA). Apple pomace and citrus peel are the raw material for commercial pectin. However, other agronomic wastes, such as sugar beet pulp (SBP), have been used to obtain pectin [1].

The most common technology to extract pectin is conventional extraction at low pH and high temperatures for a long time. However, novel techniques are being developed to improve pectin extraction, such as, for example, microwave-assisted extraction or ultrasound-assisted extraction [2].

Ultrasound-assisted extraction (UAE) has advantages over conventional extraction, such as reducing extraction time and energy consumption. When the UAE is combined with surfactants, extraction efficiency can be increased. Surfactants allow the pectin to be recovered without degradation because these substances establish chemical and physical interactions with the pectin, which remains within the micelle in the lipophilic zone [3].

Once the extraction has been performed, a pectin recovery is necessary. Commonly, alcohol precipitation is an effective method for it. However, precipitation is a non-selective process because other compounds, such as sugars, can precipitate, decreasing pectin purity [1]. Pectin extracted by UAE has a relatively high molecular weight (MW) (> 50 kDa) [4]. Therefore, ultrafiltration/diafiltration (UF/DF) membranes can concentrate and purify the liquid extract and separate the pectin from the low MW compounds. In this way, when precipitation performs after the membrane separation process, the precipitated pectin-enriched product is expected to have a higher degree of purity.

This work aims to compare different membrane configurations for the concentration and purification of a pectin-enriched extract liquid obtained in the surfactant-mediated UAE process. The raw material was SBP with a pectin concentration of 17 g GalA/100 g SBP. The pectin concentration of 5.5 g/L in the extract was reached under optimal UAE extraction conditions (surfactant concentration = 4 g Tween80/L, pH = 1, amplitude = 90%, time = 90 min and S/L ratio= 1/20 (g/mL)). After that, the liquid extract was concentrated and purified by two different membrane configurations. The membrane used for pectin recovery had a MW cut-off of 50 kDa and a filtration area of 50 cm^2 (Pellicon XL 50 Biomax membrane). The first configuration (UF/DF) consisted of the liquid extract being concentrated by ultrafiltration (UF), and the retentate was subjected to a diafiltration (DF) to purify the liquid. In the second configuration (DF/UF), the liquid extract is purified by DF and then concentrated by UF. In these cases, the transmembrane pressure (TMP) was maintained within the range of 1.5 to 2.0 bar. The feed flow rate was fixed at around 0.8 mL/min/cm^2, and the operation time was around 1 hour. Subsequently, the pectin was precipitated with ethanol. The results showed that when UF/DF configuration is used, the pectin yield is 41%, with a GalA content of 6.9 g/100 g SBP. On the other hand, for DF/UF, the pectin yield reached 57%, with a GalA content of 9.6 g/100 g SBP. Generally, both configurations are suitable for the selective recovery of pectin from SBP. However, the DF/UF sequence provides a higher yield and purity of pectin in the final precipitated product.

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Recovery of humic acids from mixed municipal waste compost with alkaline extraction

Fernández-Delgado M.[1,2*], **García-Cubero M.T.**[1,2], **Coca M.**[1,2], **Lucas S.**[1,2]

[1]Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain
[2]Institute of Sustainable Processes, Dr. Mergelina s/n, 47011 Valladolid, Spain
**marina.fernandez.delgado@uva.es*

Humic acids (HA) are large organic polymers with high molecular weight, generally obtained from humic compounds of organic matter [1]. Some applications for HA are fertilizer, potential battery material for storage energy, pollutants adsorbent, and additive in construction materials [2]. Mainly, leonardite and lignite coals are the raw material to produce the commercial HAs through an alkaline extraction, reaching purities over 90%. However, these materials are unsustainable resources, so searching for organic and environmentally friendly materials such as mixed municipal waste compost (MMWC) is necessary.

MMWC is obtained from the composting and stabilizing municipal solid waste (MSW) organic matter in the mechanical-biological treatment (MBT) plants. The EU produces nearly 250 Mt of MSW annually, so the MMWC production is high in Europe. However, MMWC cannot be used as agricultural compost due to its lousy quality and heavy metal content. In addition, only a part of the total produced MMWC can be landfilled due to increasingly stringent landfill restrictions to comply with the circular economy principle [3]. Therefore, developing alternatives for the valorization of MMWC is a significant social challenge.

Therefore, in this work, the optimization of HAs extraction from MMWC is proposed. The extraction will be performed under alkaline conditions and optimized through a response surface design. For this, two stages were proposed: the first, the conventional alkaline extraction using NaOH as a solvent and the second, the precipitation of HAs using 6 M HCl. The operating extraction conditions for the experimental design, selected based on previous experimentation, were: temperature (30 - 60 ºC), solid/liquid ratio (10 - 40% w/v), and NaOH concentration (0.25 and 1 M). In all runs, the extraction time (24 h) and the agitation (200 rpm) were fixed. The response variables to be optimized were the purity of the humic acids (g TOC_{HA}/g precipitated solid) and the organic carbon recovery yield (g TOC_{HA}/g $TOC_{\text{extract liquid}}$). Experiments were performed in duplicate.

After optimizing the proposed design of experiments with Statgraphics Centurion XVIII version, the optimal extraction conditions with the desirability of 100% were obtained. The optimized conditions were: temperature: 40 ºC, solid/liquid ratio: 37% w/v, and NaOH concentration: 1.2 M. In these conditions, the HA purity was 0.58 g TOC_{HA}/g precipitated solid and 0.86 g TOC_{HA}/g $TOC_{\text{extract liquid}}$. These values are similar to HAs extracted from fish waste and sugarcane bagasse co-compost with 0.1 M NaOH, reaching a purity of 0.51 g TOC_{HA}/g precipitated solid [4].

Therefore, MMWC is a promising raw material for HA recovery using conventional alkaline extraction under mild operating conditions. The proposed process is suitable for the valorization of this waste, contributing to principles for a sustainable circular economy.

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Ecofriendly extraction of phenolic compounds from Galician hop (*Humulus lupulus* L.) leaves using deep eutectic solvents

A. Rubira[1], F. Rebelo[1], E. Falqué[2], R. Yáñez[1,3], G. Eibes[4], B. Gullón[1,*]

[1]Department of Chemical Engineering, Faculty of Science, University of Vigo (Campus Ourense), As Lagoas s/n, 32004 Ourense, Spain
[2]Department of Analytical Chemistry, Faculty of Science, University of Vigo (Campus Ourense), As Lagoas s/n, 32004 Ourense, Spain
[3]Biomedical Research Centre (CINBIO), University of Vigo, University Campus As Lagoas-Marcosende, 36310 Vigo, Spain
[4]CRETUS Institute, Department of Chemical Engineering, Universidade de Santiago de Compostela, Santiago de Compostela, 15706 A Coruña, Spain
Correspondence: bgullon@uvigo.es

The hop (*Humulus lupulus* L.) is mainly used in the brewing industry to confer beer its characteristic bitterness, aroma and flavour. Apart from this use, hop cones have been traditionally used in medicine for controlling spasms, anxiety, fever, inflammation, activation of gastric functions and sleeping disorder treatments, among others [1]. The industrial cultivation of hops generates large amounts of unexploited by-products and residues, such as stems and leaves, which currently lack value-added applications [2]. However, these wastes constitute a remarkable natural source of valuable bioactive compounds. Therefore, their revalorization could be an interesting strategy to promote the transition towards a more efficient circular model.

Traditionally, most of the studies concerning the extraction of bioactive compounds from several food matrices have been conducted using conventional organic solvents, like methanol, ethanol, acetone, diethyl ether or ethyl acetate. However, these solvents are associated with environmental problems and can be harmful to health if traces remain in the extracts. Hence, the search for greener and safer alternatives for the extraction of bioactive compounds is imperative. Over the last few years, deep eutectic solvents (DES) have been proposed as a green alternative to conventional solvents. DESs are considered suitable solvents for foods, cosmetics and pharmaceuticals due to their excellent properties such as biodegradability, low toxicity, solute stabilization, sustainability and low cost [4].

This study assessed for the first time the extraction of polyphenolic compounds from hop leaves via solid-liquid extraction using deep eutectic solvents. For this purpose, the effect of five different DES systems on polyphenol extraction was explored and compared to the results of a hydroethanolic solution (50% v/v) as a benchmark.

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Selective fractionation of olive tree prunings using partially immiscible mixtures of water and alcohols

S. Rivas[1*], P. Reboredo-Rodríguez[2], M. Figueiredo-González[2], C. González-Barreiro[2], B. Cancho-Grande[2], R. Yáñez[1], J.L. Alonso[1], A. Moure[1], H. Domínguez[1]

[1] Chemical Engineering Department, University of Vigo (Campus Ourense), Faculty of Sciences, Polytechnical Building, As Lagoas 32004 Ourense, Spain
[2] Food and Health Omics, Department of Analytical and Food Chemistry, Faculty of Science, University of Vigo – Ourense Campus, 32004 Ourense, Spain
**sandrarivas@uvigo.es*

Olive tree prunings (OTP) are lignocellulosic wastes from agriculture. Usually, OTP are burned or left in the fields as fertilizer, although these alternatives involve environmental problems and, in any case, an added management problem for the farmer [1]. As alternative, OTP can be reused as raw material for the development of sustainable processes that, following the philosophy of biorefinery, allow the fractionation of the main constituents and further individualized valorization to obtain bio-products and/or biofuels. However, fractionation of lignocellulosic biomass is complex, due to the heterogeneous nature of the constituents: polysaccharides (cellulose and hemicelluloses) and non-saccharide ones (lignin, extractives, etc.) [2]. Pretreatment processing optimized for an integral biorefinery should: a) exhibit selective separation of each constituent, b) offer easy access to the constituents; c) allow recovery of each constituent in high yield, d) give process components ready for conversion to biochemicals [3]. In this context, organosolv pretreatments can meet these requirements.

This work proposes an organosolv strategy for the selective separation of OTP constituents (cellulose, hemicelluloses and lignin) using mixtures of water and hydrophobic solvents. [2, 4]. Microwave heating technology was considered for its improved efficiency, based in fast heating profiles, easy operation, homogeneous heating and efficient control [2]. OTP were previously subjected to extractives removal (ethanol 90%, at room temperature for 30 minutes) and valorization. Then, free-extractive OTP (FE_OTP) were treated with mixtures of water/1-pentanol at a liquid to solid ratio of 10 mL of liquid/g of FE_OTP, by microwave heating. The selected variables were: temperature (140 - 170°C), reaction time (10-30 minutes), percentage of catalyst (1 - 2% of sulphuric acid, respect the solid), and aqueous: organic ratio (v:v) of 1:1 and 0.66:1.

The results of the organosolv pretreatment on FE_OTP demonstrate the selective solubilisation of hemicelluloses in the aqueous phase, the partial solubilisation of lignin in the organic one, while the highest proportion of cellulose remains in the spent solid. The influence of the aqueous:organic ratio, temperature and amount of catalyst was demonstrated, reaching delignification values of 75%, almost complete solubilisation of hemicelluloses and a rich-cellulose processed solid (about 80% of cellulose content). In all experiments, partial constant loss of cellulose was observed, that was solubilized in the aqueous liquid phase together with hemicelluloses, reaching high concentrations of sugars in form of poly- oligo- and/or monosaccharides.

Acknowledgments

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Solubilization of hemicelluloses and lignin from Robinia wood via microwave-assisted autohydrolysis and delignification with deep eutectic solvents (DES)

Alba Pérez-Pérez[1],*, Álvaro Lobato[1], Beatriz Rodríguez-Martínez[1], Fernando Rodríguez-Rebelo[1], Beatriz Gullón[1], Aloia Romaní[1], Gil Garrote, Pablo G. del Río[1,2]

[1]Department of Chemical Engineering, Faculty of Science, University of Vigo (Campus Ourense), As Lagoas, 32004 Ourense, Spain
[2]Stokes Laboratories, School of Engineering, Bernal Institute, University of Limerick, Limerick V94 T9PX, Ireland
**alba.perez.perez@uvigo.es*

Nowadays, the increasing use of limited non-renewable resources as a consequence of the ever-increasing human demands, has led to the need to search for sustainable alternatives based on renewable sources to reduce or eliminate the problems resulting from the dependence on fossil fuels [1]. Robinia pseudoacacia is a type of lignocellulosic biomass characterized by rapid growth, high biomass production and high resistance to extreme conditions. As a lignocellulosic material, the wood of this species can be fractionated following a biorefinery scheme for the production of different value-added compounds (chemicals, materials, fuels, bioenergy, etc.). However, in order to take advantage of each of its fractions, it is necessary to break its recalcitrant structure through different pretreatment stages. Firstly, microwave-assisted autohydrolysis is a sustainable technology that allows a fast and efficient removal of hemicelluloses, providing a solid mostly composed of cellulose and lignin [2]. Secondly, the lignin solubilization via novel solvents such as deep eutectic solvents (DES) present some advantages such as low or null toxicity, recyclability, availability, easy synthesis and low price [3 and 4].

The main objective of this study was the coupling of different technologies (microwave-assisted autohydrolysis and DES delignification) for the optimal extraction of hemicelluloses and lignin. The efficient lignin extraction of the previously autohydrolyzed solids was screened and, subsequently, the optimization of the delignification conditions, such as the molar ratio of the solvents and the reaction temperature and time.

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BECCSU con captura de simulación de procesos hacia la sustentabilidad

Cristina Garcia Gonzalez[,*], Shoeib Faraji Abdolmaleki[1], Vaisakh Yesodharan[1], Pastora M. Bello Bugallo[1]

[1] *TECH-NASE Research Group, School of Engineering (ETSE) Universidade de Santiago de Compostela Avda. Lope Gomez de Marzoa s/n 15782, Santiago de Compostela, Spain*
**e-mail: cristina.garcia.gonzalez@rai.usc.es*

Abstract

El diseño y la definición de sistemas de captura y almacenamiento/utilización de carbono (CCSU) para centrales eléctricas que generan electricidad a partir de la combustión de materias primas incluyen procesos sensibles, costosos y que requieren mucho tiempo. Por otro lado, la importancia de seleccionar tecnología sustentable es crítica particularmente en términos de emisiones industriales. Por lo tanto, para garantizar la gestión responsable de los recursos naturales, se debe centrar la intervención en las fuentes y establecer un marco amplio para regular las operaciones industriales significativas. Además, si corresponde, tenga en cuenta las circunstancias económicas y las características locales únicas del sitio donde se lleva a cabo la actividad industrial [1]. En este sentido, las plantas de energía de biomasa son comparables a las plantas de combustibles fósiles en el sentido de que ambas generan electricidad al quemar una materia prima. Como resultado, las plantas de biomasa plantean cuestiones sobre las emisiones al aire y el consumo de agua que son comparables, pero no idénticas, a las planteadas por las plantas de combustibles fósiles. La materia prima de la planta de biomasa también puede producirse de manera sostenible, mientras que los combustibles fósiles no son renovables. Cuando se utiliza biomasa para generar electricidad, el tipo de materias primas tiene un impacto sustancial en el uso de la tierra y las emisiones de calentamiento global del ciclo de vida ([2-5]).

Este estudio tiene como objetivo encontrar bioenergía más sostenible con tecnologías CCSU (BECCSU) al observar varios procesos y considerar metodologías variadas. La simulación de procesos se utilizará como una herramienta para medir la salida de cada proceso de captura. Ayuda a comparar diferentes geometrías y tipos de estructuras posibles para el proceso de captura. Para iluminar una mayor sostenibilidad, sigue un marco de pensamiento sistémico y permite una integración intersectorial optimizada.

La diversidad de procesos de la BECCSU se examina primero en este trabajo empleando plataformas digitales. Los criterios en la sección de sustentabilidad para la bioenergía luego se analizan y categorizan usando el concepto de sustentabilidad. Finalmente, dependiendo de las características de sostenibilidad, se compararán y profundizarán los resultados de cada técnica de la BECCSU a partir de la simulación de procesos.

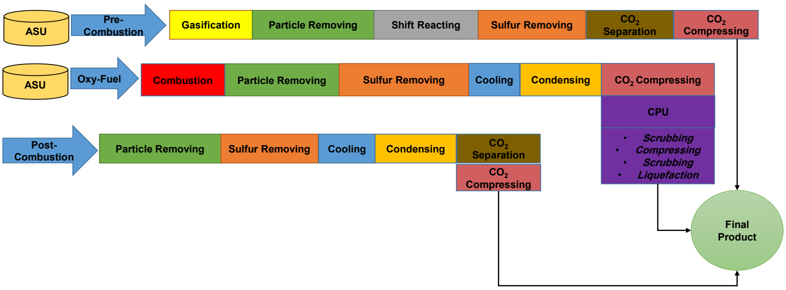

Fig.1. Tres procesos principales de secuestro de carbono en bioenergía y sus componentes operativos

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Optimizing spray drying conditions for green extracts from a commercial hop variety

T. Ferreira-Anta[1], N. Flórez Fernández[1*], J.M. Vilariño[2], M. D. Torres[1], Herminia Domínguez[1]

[1] CINBIO, Universidade de Vigo, Departamento de Ingeniería Química, Campus Ourense, 32004 Ourense, Spain
[2] R&D Department, Hijos de Rivera, S.A.U. c/ José María Rivera, nº6, A Coruña, Spain
**noelia.florez@uvigo.es*

Nowadays, consumer demand for natural ingredients is growing. Botanical species, such as hops, are a potential source of bioactive compounds and these have received increased interest of the scientific community [1]. Among these compounds are phenolics, some of them show antimicrobial, antifungal or antioxidant properties, which broadens its future applications [2]. The efficiency in solid-liquid extraction, can not only offer increased yields, but also can enhance the quality of the final products [3]. On the other hand, spray drying offers economic and operational advantages that can be applied in the industry [4]. In this context, the objective of this work was to evaluate the drying yield using different conditions for an aqueous extract of a variety of hop.

The Nugget hop variety was kindly provided by Hijos de Rivera S.A. (A Coruña, Spain). The extraction of phenolic compounds was performed using ultrasound-assisted extraction (US) in a water bath under previously optimized operating conditions. The solid:liquid ratio was fixed at 1:15 (w/w), the solvent used was distilled water at 55 °C for 120 minutes. After filtration, the total phenolic content (TPC) of the liquid extract was analyzed and *in vitro* antiradical capacity values were determined as Trolox equivalent (TEAC), both at least in triplicate. The soluble extracts were dried by atomization using a spray-dryer. The equipment used was a BÜCHI B-290 (Flawil, Switzerland) equipped with a standard cyclone and a 1.5 mm nozzle. The operating conditions were selected according to scientific literature [5], assessing five drying temperatures between 110 and 150 ºC. The yield of the process was also measured by gravimetry.

Total phenolic content and antioxidant capacity were 13.3 mg equivalent of acid gallic/g of extract and 26.2 mg of Trolox/g extract, respectively. The attained yields were above of 50% for all cases (66.5-77.1%), being the highest yield value corresponding to the temperature of 130 ºC and the lowest to 140 ºC. The next step could be to study the behavior of the extracts to formulate polymeric microparticles with the aim to protect/preserve bioactive compounds.

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Bioactive Phenolic Compounds Extraction from Avocado Peels employing Deep Eutectic Solvents

Beatriz Rodríguez-Martínez[1*], **Pedro Ferreira-Santos[2,3]**, **Irene Méndez Alfonso[1]**, **Sidonia Martínez[1]**, **Zlatina Genisheva[2,3]** and **Beatriz Gullón[1]**

[1]Department of Chemical Engineering, Faculty of Science, University of Vigo (Campus Ourense), As Lagoas, 32004 Ourense, Spain
[2]Centre of Biological Engineering, Universidade do Minho, 4710-057 Braga, Portugal
[3]LABBELS—Associate Laboratory, 4710-057 Braga, Portugal
**beatriz.rodriguez@uvigo.es*

The industrial processing of avocado generates a large amount of waste where avocado peels are the main one [1]. Due to its richness in bioactive compounds like phenolic compounds, this by-product has increased its interest in the pharmaceutical and food industries in the last 10 years [2]. The current demand of more sustainable processes for the recovery of high-value compounds encourages the extraction of bioactive compounds using deep eutectic solvents (DES) as an alternative to conventional toxic solvents. DESs show interesting properties such as short preparation time, biocompatibility, easy storage, biodegradability, low cost, non-flammability, high extraction capacity, non-toxicity, and environmentally friendly which make them more attractive than traditional solvents [3].

In the present work, five DES were employed for bioactive phenolic compounds extraction from avocado peels. The content of total phenolics (TPC) and flavonoids (TFC) was measured to determine the extraction efficiency. All DES employed presented higher extraction efficiencies than ethanol and the best results were obtained with choline chloride - acetic acid (DES 2) (92.03 ± 2.11 mg GAE/g DAP for TPC and 186.01 ± 3.27 mg RE/g DAP for TFC), and choline chloride - lactic acid (DES 5) (92.09 ± 4.92 mg GAE/g DAP for TPC and 211.73 ± 1.50 mg RE/g DAP for TFC). The most representative class of phenolic compounds found in avocado peel extract were flavonoids (like catechin, rutin, and epicatechin), and phenolic acids such as gallic, ferulic, and hydroxybenzoic acids. Moreover, all DES extracts have greater antioxidant activity (FRAP: 72.5–121.1 mg TE/g; TAC: 90.0–126.1 mg AAE/g) than ethanol extracts. Thanks to these results, coupled with the non-toxic, biodegradable, low-cost, and environmentally friendly characteristics of DESs, provide strong evidence that DESs represent a better alternative to organic solvents for the recovery of phenolic bioactive compounds from agro-industrial wastes like avocado peels.

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Potato peels waste as a sustainable source for biotechnological production of biofuels using very high gravity strategies

Beatriz Rodríguez-Martínez[1*], Eduardo Coelho[2,3], Beatriz Gullón[1], Remedios Yáñez[4,5] and Lucília Domingues[2,3]

[1]Universidade de Vigo, Departamento de Enxeñaría Química, Facultade de Ciencias, As Lagoas, 32004 Ourense, Spain
[2]Centre of Biological Engineering, Universidade do Minho, 4710-057 Braga, Portugal
[3]LABBELS—Associate Laboratory, 4710-057 Braga, Portugal
[4]Universidade de Vigo, Departamento de Enxeñaría Química, Escola de Enxeñaría Industrial, Campus Lagoas-Marcosende 9, Vigo, 36310, Spain
[5]CINBIO, Universidade de Vigo, 36310 Vigo, Spain
**beatriz.rodriguez@uvigo.es*

Potatoes industrial processing generate large quantities of residues, mainly peels. Due to their high content in polysaccharides (mostly starch) and minerals and their low cost, these by-products can be used as an alternative raw material to obtain second-generation bioethanol employing very high gravity strategies [1,2].

In this study, firstly, liquefaction and enzymatic hydrolysis stages were optimized in order to know their influence on the final concentration of glucose. With this purpose, several parameters were evaluated, including the effect of two commercial glucoamylase enzymes (SAN Super® 360 L or Saczyme® Yield), the loading of these enzymes, the loading of a commercial pectinase enzyme (Viscozyme® L) and the possibility of adding the solid in one or several loads.

Subsequently, the presaccharification and fermentation stage was studied. For this purpose, the two previously mentioned glucoamylases and two robust and thermotolerant yeasts (a strain of *Saccharomyces cerevisiae* Ethanol Red® and *Kluyveromyces marxianus S9* isolated from cocoa fermentation [3]) were evaluated at two different temperatures (37 - 42 °C). The very high gravity strategies proposed allowed to reach intermediate to high ethanol concentrations (between 40-100 g/L) without the addition of external nutrients. These results compare favorably with other technologies and allow validating this method for the proposed raw material, thus optimizing the process for obtaining bioethanol.

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Delignification of autohydrolyzed *Acacia dealbata* wood using carboxylic acid-based deep eutectic solvents (DESs)

Álvaro Lobato-Rodríguez[1,*], Alba Pérez-Pérez[1], Beatriz Rodríguez-Martínez[1], Fernando R. Rebelo[1], Beatriz Gullón[1], Pablo G. del Río[1,2], Aloia Romaní[1], Gil Garrote[1]

[1]Department of Chemical Engineering, Faculty of Science, University of Vigo (Campus Ourense),
As Lagoas 32004, Ourense, Spain
[2]Stokes Laboratories, School of Engineering, Bernal Institute,
University of Limerick, Limerick V94 T9PX, Ireland
**alvaro.lobato@uvigo.es*

Lignocellulosic biomass (LCB) is considered the cheapest and most abundant renewable resource worldwide, displaying a great potential to manufacture high-added-value products and biofuels [1]. Specifically, *Acacia dealbata* is an invasive angiosperm that is underexploited and whose distribution causes structural modifications in native ecosystems [2]

On the other hand, fractionation of the main constituents of LCB in separated streams is key to provide a more efficient valorisation [3]. Hydrothermal pretreatment or autohydrolysis is proposed as a sustainable first step to selectively solubilize hemicelluloses, especially in form of oligosaccharides, without using corrosive, expensive and toxic chemical reagents [4]. To valorise the lignin fraction and increase the enzymatic digestibility of the remaining solid, a second step based on delignification processes using carboxylic acid-based deep eutectic solvents (DES) was studied. DES are liquid mixtures that have been outlined as a new generation of safe green solvents and are composed of hydrogen-bond acceptors (HBAs, commonly using chlorine chloride due to its low cost and safe and healthy nature) and hydrogen-bond donors (HBD) [5,6]

This work aims to evaluate the delignification of autohydrolyzed *Acacia dealbata* wood with three binary carboxylic acid-based DES. These solvents were synthesised with chlorine chloride (ChCl) as HBA and formic acid (FA), lactic acid (LA) and acetic acid (AA) as HBDs with a 1:2 molar ratio. The process was performed at RLS = 15 g DES/g MLC at 130 ºC for 2 h. Delignification yields of 29%, 37% and 38% were achieved using ChCl:LA (1:2), ChCl:FA (1:2) and ChCl:AA (1:2), respectively. Based on the study carried out by Oh et al. [7], a ternary DES was synthesized by combining the two binary DES that achieved a higher delignification yield to increase it, resulting in a 51% of delignification using ChCl:AA:FA (1:1:1).

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Deslignificación de madeira de *Paulownia* utilizando disolventes eutécticos profundos

Fernando R. Rebelo[1*], Pablo G. del Río[1,2], Beatriz Gullón[1], Beatriz Rodríguez-Martínez[1], Álvaro Lobato-Rodríguez[1], Alba Pérez-Pérez[1], Aloia Romaní[1], Gil Garrote[1]

[1]Departmento de Enxeñaría Química, Facultade de Ciencias, Universidade de Vigo (Campus Ourense), As Lagoas, 32004 Ourense, España
[2]Stokes Laboratories, School of Engineering, Bernal Institute,
University of Limerick, Limerick V94 T9PX, Ireland
**frodriguez@uvigo.gal*

O continuo aumento da demanda global de enerxía na historia recente motivou a necesidade de diversificar a súa obtención. Así, ó longo das últimas décadas, os recursos tradicionais para obtela fóronse complementando ou substituíndo por ouros capaces de adecuarse aos requirimentos actuais da sociedade, tales como a sustentabilidade ou a mellora da eficiencia enerxética [1]. Unha destas alternativas é a bioenerxía e, concretamente, a produción de biocombustibles tales como o bioetanol, obtido da fermentación dos azucres resultantes da dixestión da celulosa presente nos materiais lignocelulósicos [2].

A *Paulownia* é unha espermatófita capaz de producir grandes cantidades de biomasa (~50 t /ha·ano) de maneira rápida, o cal a fai moi adecuada para a produción de bioetanol [3]. Para que isto sexa posible, a biomasa debe de ser pretratada adecuadamente co obxectivo separar as distintas fraccións que a compoñen e así garantir unha boa accesibilidade da celulosa, sendo a deslignificación unha das etapas máis destacables deste proceso. Historicamente, a deslignificación vense realizando por medio de disolventes orgánicos (organosolv) ou disolucións alcalinas. Porén, nos últimos anos os disolventes eutécticos profundos (DES), máis estables, baratos e menos contaminantes, están amosando un amplo potencial para levar a cabo esta tarefa, obtendo resultados comparables aos acadados ata o momento cos disolventes convencionais [4].

Así, neste traballo de investigación estudouse a utilización de dous DES formulados a base de ácido fórmico ou ácido acético, mesturados con cloruro de colina nunha relación molar 2:1 para a deslignificación de madeira de *Paulownia*: ben para a materia prima, ben tras o seu somentemento a un tratamento de autohidrólise para a liberación máxima de oligómeros hemicelulósicos. Os resultados obtidos nas probas denotan un gran potencial destes disolventes para a deslignificación da madeira de *Paulownia*, acadando valores de deslignificación do 60% para o caso da materia prima e do 72% para o sólido autohidrolizado.

Agradecementos

Fer R. Rebelo (FPU20/02385), Alba Pérez-Pérez (FPU21/02446) e Álvaro Lobato-Rodríguez (PRE2020-093359) agradecen o apoio do Ministerio de Universidades polas súas axudas predoutorais. Pablo G. del Río agradece á Xunta de Galicia pola súa axuda postdoutoral (ED481B-2022-020). Beatriz Gullón (RYC2018-026177-I) e Aloia Romaní (RYC2020-030690-I) agradecen ao Ministerio de Ciencia e Innovación polos seus contratos postdoutorais.

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Delignification assessment of vine shoots using deep eutectic solvents

A. Romaní[1*], F.J. Portela[1], P. G. del Río[1,2], G. Garrote[1], B. Gullón[1]

[1]Chemical Engineering Department, Science Faculty, University of Vigo, As Lagoas s/n CP 32004, Ourense, Spain

[2]Stokes Laboratories, School of Engineering, Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland

**corresponding author: aloia@uvigo.es*

Sustainable growth based on bio-economy aims at responding to environmental concerns, rural development, and energy security [1]. The bio-economy is based on the optimal use of renewable resources through the development of biorefineries, in compliance with the implementation of zero-waste policies, which promotes the transition towards a circular bio-economy. The wine-making sector is one of the most important agricultural activities worldwide [2], where large amounts of residues are generated during wine processing, especially pruning residues of the vine (or vine shoots). Efficient fractionation of this residue into value-added products (such as bioethanol, bioactive compounds, and high value derived lignin compounds) requires a suitable pretreatment for breaking down the recalcitrant lignocellulosic structure. In this sense, the use of cutting-edge solvents, such as deep eutectic solvents (DES), have emerged as sustainable and safe solvents to replace conventional organic solvents and alkalis employed for the delignification of lignocellulosic biomass [3,4].

In view of the above, the main objective of this work was the evaluation of different eutectic mixtures (namely, Choline Chloride [ChCl] combined with several organic acids, such as lactic acid-LA, acetic acid-AA, and formic acid-FA) on vine shoot fractionation using the following molar ratios (1:10 and 1:5).

Delignification treatments with DES were carried out in an autoclave at temperatures in the range of 120-130 ºC for times varying from 30 min to 120 min. Raw material and delignified vine shoot samples were chemically analysed following the NREL/TP-510-42618 procedures [5]. The main results obtained from delignification experiments with DES showed that the eutectic mixtures with lactic acid and formic acid yielded the highest cellulose recoveries (71-80 %). On the other hand, lower recovery of cellulose (62 %) was achieved using [ChCl:AA]. With regard to hemicellulose (composed mainly of xylan) was the most solubilized fraction, achieving 90 % of solubilisation of xylan using ChCl:FA molar ratio of 1:5 at 130 ºC for 120 min. The percentage of delignification was around 50 % in all of the conditions assayed.

Overall, the use of ChCl:FA was suitable for higher cellulose recovery and a delignification improvement of 14 % than the results obtained with acetic acid and lactic acid.

Acknowledgments

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Ultrasound-assisted depolymerization of oligocarrageenan from *Mastocarpus stellatus*

Milena Álvarez-Viñas[1], María Dolores Torres[1], Herminia Domínguez[1,*]

[1] *Departamento de Enxeñería Quimica, Universidade de Vigo (Campus Ourense), Edificio Politécnico,*
As Lagoas, 32004 Ourense, Spain
**herminia@uvigo.es*

Hybrids of carrageenans, proteins, minerals, among other compounds, have promoted interest in red algae. Due to their diverse composition, they are interesting for the study in the pharmaceutical, cosmetic and food fields. These macroalgae, such as *Mastocarpus stellatus*, display a wide range of valuable products that can present functional and biological features.

In order to obtain the maximum benefit from this seaweed, it has to be processed to separate its main components. Among the different extraction technologies, autohydrolysis, also known as subcritical water extraction (SWE), has been stated as an environmentally friendly and sustainable procedure for the fractionation of biomass. Additionally, depolymerization of carrageenan can provide compounds with higher activity and bioavailability and lower viscosity. Novel technologies such as ultrasonication can increase the biological activity in the extract, without a massive consumption of energy. This study dealt with the processing of the of *Mastocarpus stellatus* autohydrolysis extract via ultrasonic technology.

Mastocarpus stellatus, kindly supplied by Portomuíños (Pontevedra, NW Spain), was processed in a stainless steel reactor (Parr, IL, USA) with a liquid to solid ratio of 30 g/g during heating up to 130 °C following the rapid heating profile, optimal for the extraction of carrageenan. Subsequently, ultrasonic technology was applied to the autohydrolysis extract. Times from 5 minutes to 2 h, and three type of pulses were set to study the viscosity and molecular weight, aiming at producing a processed extract with potential for bioactive properties.

The results indicated a clear decrease of the viscosity with values ranging 16417-3835 Pa·s for degass, 16016-2182 Pa·s for sweep, and 1467-3956 Pa·s for pulse. In addition, the sulphate content varied between 12.78-62.58 g sulphate/100 g extract. Regarding the molecular weight distribution, the results depicted a slight rise in lower molecular weights than $2.36 \cdot 10^4$ g/mol, which suggests the necessity of increasing the harshness of the conditions (temperature, time and/or frequency). This work represents a first tentative for the depolymerisation of carrageenan from *Mastocarpus stellatus* extract to increase its bioactive features.

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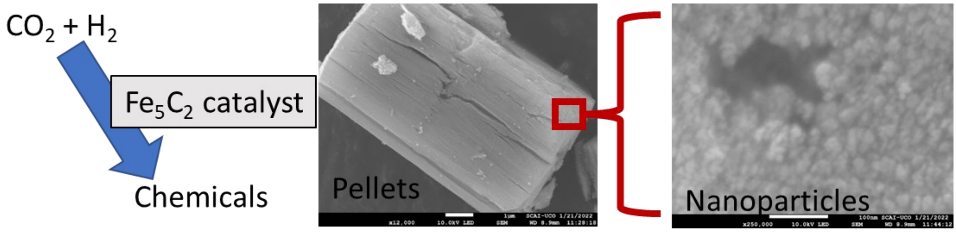
Valorization of CO2 to chemicals using iron carbides as catalyst

Pedro Muñoz[1], Montes Vicente[2*], Beatriz Ledesma[1], García Araya Juan F.[2], Rivas F. Javier[2], Juan Feliz Gonzalez[2,]

1. Department of Applied Physic, University of Extremadura, Badajoz, Spain
2. Instituto Universitario de Investigación del agua, Cambio Climático y Sostenibilidad (IACYS), Av. de la Investigación s/n, Badajoz, España
**vmontes@unex.es*

Controlar y disminuir la concentración de CO2 atmosférico es uno de los grandes retos para las próximas décadas. Su control implica, reducir, capturar y transformar dicho gas de efecto invernadero. De hecho, el CO2 podría convertirse en una materia prima renovable para la obtención de productos químicos y energía, ya que puede transformarse en productos químicos ya sea directamente o a través de la conversión de biomasa. Entre las diversas alternativas estudiadas en las últimas décadas destacan, termo-catálisis, electro-catálisis, bio-catálisis y foto-catálisis. Hoy en día el proceso se aplica industrialmente, lamentablemente solo en unos pocos lugares, debido a varios problemas, como; el envenenamiento del catalizador por el azufre presente en la biomasa o la baja conversión y por ende el costo del proceso. Los catalizadores de sulfuros, carburos y fosfuros han demostraron una excelente resistencia a los compuestos que contienen azufre y una actividad catalítica competitiva con los catalizadores metálicos tradicionales. Por lo tanto, el objetivo principal del presente estudio es examinar la actividad catalítica de diferentes Fe5C2 sobre la reducción térmica y la fotorreducción de CO2. El objetivo es obtener biocombustibles o productos químicos con valor añadido y comprender mejor las vías y mecanismos de las reacciones involucradas.

Los catalizadores se sintetizaron usando glucosa o glicerol como fuente de carbono, y nitrato de Fe, mediante reflujo. El sólido obtenido fue lavado y activado con CO a 350 ºC antes delos test catalíticos. Los sólidos exhibieron actividad catalítica en la reducción de CO2, ya sea en condiciones térmicas y fotocatalíticas. La condición térmica dio como resultado una conversión mucho mayor en comparación con la fotoactivación, 3,3 mL/min*gcat CO2 y 0,003 mL CO2/h*gcat, respectivamente, conversiones que están similares a las descritas en literatura [1] y [2]. En las reacciones térmicas, la baja conversión incrementó la fracción de hidrocarburo líquido y sólido obtenido, lográndose distribuciones de cadenas carbonadas entre 6 y 32 átomos de carbono. Bajo activación lumínica, los principales productos fueron CH4 (60%) y CO (38%).



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How the addition of polyphenols from *Ascophyllum nodosum* seaweeds affects to corn starch gels rheology

L. Montes[1], M. Santamaria[2], R. Garzon[2], C.M. Rosell[2,3], R. Moreira[1*]

[1]Chemical Engineering Department, Universidade de Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15780 Santiago de Compostela, Spain
[2]Institute of Agrochemistry and Food Technology (IATA-CSIC). C/Agustin Escardino 7, 46980 Paterna, Spain
[3]Department of Food and Human Nutritional Sciences. University of Manitoba, Winnipeg, Canada
ramon.moreira@usc.es

Gluten-free products are in high demand as more people are diagnosed as having celiac disease. A gluten-free diet can promote a high glycemic index, therefore, a high relationship between type 1 diabetes and celiac disease exists [1]. Commonly, to improve the gluten-free products hydrocolloids are used but the aim of this work is improving the gluten-free products with polyphenols (PP) from *Ascophyllum nodosum* seaweeds which have many health benefits due to their antioxidant power offering protection against development diabetes [2].

Corn starch (CS) gels were made at two starch concentrations (1.95 and 5.0% w/w). For 1.95 % w/w samples, the PP/CS ratios were: 0, 0.5, 2.5 and 5.0; while for gels at 5.0% w/w the ratios were: 0, 0.2, 0.9 and 1.9, adding different amounts of PP solutions of 0, 0.1, 0.5 and 1.0 g/L. The rheological characterization was performed with stress-controlled rheometer (Anton Paar 301) with plate-plate geometry (50 mm) and a gap of 0.25 mm. All the samples were covered with light paraffin oil to prevent water evaporation. First, a pre-shear (100 s^{-1} and 75 min) was made for the adsorption of PP in starch. Then, a heating ramp from 25 to 90ºC (at 5°C/min) was carried out followed by a time sweep at 90ºC (30 min), a cooling ramp from 90 to 25ºC (at 3°C/min) and a time sweep at 25ºC (30 min) at a constant strain of 10% and a frequency of 1 Hz (inside LVR). Finally, a frequency sweep from 0.01 to 10 Hz was made at 10% of strain and 25ºC. Temperature was controlled by a Peltier system

Above gelatinization temperature (ranged between 70 and 73ºC) the gel was formed characterized by elastic modulus greater than the viscous modulus (G´ > G´´) for all samples. In the heating ramp the addition of PP enhanced the elastic character of the samples (higher G´) independently of starch content. During the time sweep at high temperature (90 ºC) the behavior was like the previous step, the PP addition increased G´ values. However, in the cooling profile, it was observed how the G´ values of the samples with PP have lower G´ values, indicating that the presence of PP delays the rapid retrogradation of the starch gel [3]. This behavior was observed for all samples except those corresponding to the lowest PP/CS at high starch content (5% w/w).

During the maturation step at low temperature (25 ºC) the previous behavior was enhanced. Finally, the frequency sweep showed a clear drop in G´ values of low starch content gels (1.95% w/w) from 39.6 to 26.7 Pa (at 1 Hz) with increasing PP/CS (from 0 to 5). However, for starch gels at 5% w/w, a different behavior was observed. Only at high ratio PP/CS (1.9) the G´ drop was observed, while gels with low PP/CS (< 0.9) no significant differences (in G´ and in damping factor G´´/G´) with control were found. These results indicated that the rheological behavior of starch gels was modified only when a threshold PP/CS ratio was achieved, and its value increased with increasing the starch content of gel (or strength).

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IND39

Determinación de la curva de Destilación ASTM D-86 de una gasolina comercial

E.V. Lucero Baldevenites[1,2*], A.M Gayol González[3], J.C. Lucero Freites[4], L. Giménez[4]

[1]Universidad de Las Palmas de Gran Canaria, Departamento de Ingeniería Mecánica, Facultad de Ingeniería, Las Palmas de Gran Canaria, España
[2]CPES Santa Catalina (Institutos Diocesanos), Las Palmas de Gran Canaria, España
[3]Universidade de Vigo, Departamento Física Aplicada, Grupo FA2, Ciencias del Mar, Lagoas-Marcosende Vigo, España
[4]Universidad Nacional de Cuyo, Facultad de Ciencias Aplicadas a la Industria, Mendoza, Argentina.
**viviana.lucero@ulpgc.es*

Palabras clave: destilación ASTM D86, combustibles, nafta, temperatura.

El ensayo de destilación ASTM D-86 es un método que se aplica a gasolinas naturales, destilados livianos y medios del petróleo. Caracterizando a los combustibles al permitirnos determinar la volatilidad, el comportamiento en el sistema de combustión y su relación con el funcionamiento del motor, entre otras propiedades.

En el presente trabajo se exponen los resultados de las pruebas realizadas a una nafta comercial aplicando el método ASTM D86-04 [1]. Los datos obtenidos permitieron caracterizar el combustible y realizar comparaciones con las especificaciones técnicas brindadas por el proveedor [2], arribando a diversas conclusiones [3], relacionadas con su eficiencia.

Para la ejecución de estas prácticas se trabajó con una unidad de destilación manual de laboratorio (Figura 1). La muestra destila como una mezcla de hidrocarburos cuyos puntos de ebullición van en aumento, permitiendo el equipo obtener correlaciones entre temperaturas y fracciones de destilado.

Para poder trazar la curva de destilación ASTM D86 (Figura 2), es necesario realizar 2 correcciones, una relacionada con la presión real a la que se realiza el ensayo, aplicando la ecuación de Sydney-Young [4] y otra relacionada con las pérdidas de producto durante el análisis [5].

Fig. 1. Destilador ASTM D-86 manual

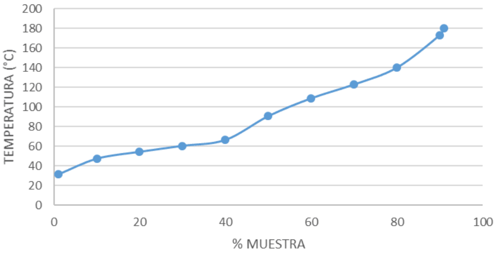

Fig. 2. Curva de destilación ASTM D-86 Nafta

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Ensayo mecánico de dobladura de un acero F-1120
Práctica de laboratorio

E.V. Lucero Baldevenites[1,2*], **A.M Gayol González**[3]

[1]Universidad de Las Palmas de Gran Canaria, Departamento de Ingeniería Mecánica, Facultad de Ingeniería, Las Palmas de Gran Canaria, España
[2]CPES Santa Catalina (Institutos Diocesanos), Las Palmas de Gran Canaria, España
[3]Universidade de Vigo, Departamento Física Aplicada, Grupo FA2, Ciencias del Mar, Lagoas-Marcosende Vigo, España
viviana.lucero@ulpgc.es

Palabras clave: ensayo, acero, Norma UNE, probeta, grietas.

El ensayo de doblado es un ensayo de tipo tecnológico, estático y destructivo, cuyo objetivo es estudiar las características de plasticidad de los materiales metálicos. Esta práctica se ha llevado a cabo teniendo en cuenta la Norma UNE-EN ISO 5173:2011 [1].

En el presente trabajo se exponen los resultados del ensayo realizado a un acero F-1120 [1]. Los datos obtenidos permitieron caracterizar la probeta a ensayar (acero F-1120) con las especificaciones técnicas brindadas por la respectiva norma [3].

Para la realización de esta práctica se trabajó con la Máquina Universal de Ensayos (Figura 1) ubicada en el Laboratorio de Ciencia de los Materiales de la ULPGC.

Se han ensayado dos probetas. En la primera se observó la aparición de grietas en la parte exterior y en los laterales de la curva, donde los esfuerzos de tracción fueron más elevados, lo que denota que las propiedades plásticas de la misma no son las deseables [2]. En la segunda se observó la no aparición de grietas lo que denota una buena capacidad de deformación plástica.

En la figura (Figura 2) se observa cómo la probeta comienza a doblarse y también se observa cómo el cordón de soldadura no se despega, lo que denota una buena pericia del soldador.

Fig. 1. Máquina Universal de Ensayos

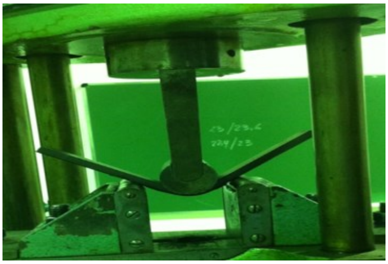

Fig 2. Comienzo del doblado de la probeta

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Extração de aromas para o desenvolvimento de kits aromáticos associados ao vinho

Camila Maria Bazzanella[1,*], Maria João Sousa[2,3], António Castro Ribeiro[2,3]

[1]Universidade Tecnológica Federal do Paraná, Agronomia, Dois Vizinhos-PR, Brasil
[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[3]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
*camilamariabazzanella@gmail.com

A extração de aromas e a sua disponibilização para treino do olfato e memorização é de fundamental importância nas áreas alimentares e em particular na área da enologia. Os aromas associados ao vinho são importantes para auxiliar os profissionais do setor a identificar aromas associados a diferentes perfis, castas presentes, tipicidade, tecnologias de produção, assim como alterações que possam ocorrer durante o processo de fabrico e/ou de estágio.

O objetivo deste trabalho foi extrair óleos essenciais a partir de plantas (folhas, caules, frutos, flores, etc.) e outras substâncias com aromas associados ao vinho para desenvolver um kit aromático.

Foram extraídos, os óleos essenciais por hidrodestilação, utilizando o aparelho de Clevenger, de acordo com a farmacopeia europeia. Foram escolhidas preferencialmente plantas em plena floração, e material fresco com o objetivo de obter os perfis de voláteis mais completos e com maior rendimento. As amostras foram extraídas durante os meses de março a junho. Foram extraídos os óleos essenciais das seguintes espécies vegetais: acácia (*Acacia longifolia*), alecrim (*Rosmarinus officinalis*), alfazema (*Lavandula angustifolia*), café (*Coffea arabica*), camomila (*Matricaria recutita*), canela (*Cinnamomum verum*), carvalho francês (*Quercus robur* L.), cedro (*Cupressus lusitanica*), choupo (*Populos nigra*), coentro (*Coriandrum sativum*), cravo (*Syzygium aromatico*), erva de São Roberto (*Geranium robertianum* L.), esteva (*Cistus ladanifer*), folha e fruto do limoeiro (*Citrus limon*), noz moscada (*Myristica fragans*), pimenta (*Piper nigrum*), pinheiro bravo (*Pinus pinaster*) e o tomilho (*Thymus zygys*).O rendimento em óleo essencial variou entre 2,97%, para o fruto da noz moscada, e 0,016 para as folhas e inflorescência do choupo.

Para avaliar a proximidade e intensidade dos aromas, foram realizadas análises sensoriais por um painel de 35 pessoas de ambos os sexos com idades compreendidas entre os 18 e os 63 anos. A maioria dos aromas apresentaram proximidade e intensidade maiores que 50%. Os aromas que apresentaram maior intensidade foram o de folha do limoeiro, casca do limão e o de canela. Os menos intensos foram o coentro, erva de São Roberto e cedro. Em relação à proximidade dos aromas, os mais próximos foram de canela, baunilha e limão e os menos próximos foram de erva de São Roberto, coentro e cedro.

Com este processo foi possível desenvolver um kit de voláteis de origem terpénica, estável para utilização com fins pedagógicos e profissionais na área da enologia. A utilização de um processo químico simples e verde, sem utilização de solventes permitiu a extração de voláteis com elevada proximidade ao aroma de referência, ideal para o objetivo.

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Potencialidad de la lignina en la mejora técnica y medioambiental de las carreteras

Pedro A. Calvo[*], **José L. Francisco**[2]

[*,2]ENCE ENERGÍA Y CELULOSA, Biofábrica de Pontevedra, Pontevedra, España
**pcalvo@ence.es*

La mayoría de los firmes de carreteras se construyen a base de hormigón asfáltico, una mezcla de piedras seleccionadas en tamaño y calidad (árido) y betún o asfalto, que es el ligante que une dichas piedras. Las condiciones de manipulación (altas temperaturas) y los agentes externos durante su vida de servicio (tráfico, temperatura extremas, lluvia, derrames químicos, movimientos geológicos…) alteran negativamente sus propiedades, deteriorándolos.

Entre las causas y los efectos del envejecimiento de los betunes, podemos citar [1]:

- Pérdida de volátiles → rotura sol-gel, variación proporción componentes, generación de interacciones y repulsas.
- Oxidación de moléculas → hidrógenos bencílicos y sulfuros alifáticos se transforman en carbonilos y sulfóxidos, variación de polaridad e interacciones
- Fotodegradación → creación de radicales libres y propagación de reacciones de rotura o condensación de cadena.

La lignina ayuda a mantener las propiedades del asfalto, disminuyendo el deterioro y minimizando costes de mantenimiento [2]:

- Disminuye la temperatura de trabajo del betún → menor degradación térmica y mayor ahorro energético.
- Ligante natural con interacciones polares- no polares → estabiliza emulsiones, retrasa la pérdida de volátiles.
- Estabilizante UV → su estructura absorbe los radicales libres generados y corta las reacciones de propagación.
- Soporta mejor la oxidación molecular → ¿actuación como material de sacrificio?

Diversas experiencias ya realizadas [2,3] demuestran la idoneidad de la lignina en la mezclas con betunes.

Maltaweg, North Sea Port, Vlissingen (Flushing) Nov. 2020. First road with all 3 asphalt layers containing kraft lignin. The middle and base layer additionally contained recycled asphalt

N987, Siddeburen, Groningen, May 2021
First road ever with both Kraft lignin and Avantium dawn lignin in 250 m long top layer sections

Fig. 4. Carreteras construidas empleando una mezcla lignina-betún 1:1 (Fuente: JUNGINGER, M.; Lignocost 2020).

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NANOQUÍMICA Y NANOTECNOLOGÍA

New architectures in soft materials for combined cancer therapy: multifunctional dehydrodipeptide-based lipogels with magneto-plasmonic properties

Valéria Gomes[1,*], Sérgio R. Veloso[2], Loic Hilliou[3], Paula M.T. Ferreira[1], Elisabete M.S. Castanheira[2]

[1]Centre of Chemistry (CQUM), University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[2]Physics Centre of Minho and Porto Universities (CF-UM-UP), 4710-057 Braga, Portugal
[3]Institute for Polymers and Composites/I3N, Department of Polymer Engineering, University of Minho, Campus de Azurém, Guimarães, Portugal
**alcindavaleria@hotmail.com*

Peptide-based hydrogels constitute an important class of biomaterials with a wide range of applications, including drug delivery, tissue engineering, *in vivo* imaging, and template materials [1,2]. In addition to their intrinsic responsiveness to physiologically important stimuli (such as pH), the incorporation of magneto-plasmonic core/shell nanoparticles allows their concentration in the desired area of the patient's organs by magnetic forces, enabling the guided transport of biologically active molecules, most of them toxic and with systemic side effects. In fact, a promising application of these nanosystems in combined cancer therapy is anticipated, through magnetically guided drug delivery and optical/magnetic hyperthermia [3]. Furthermore, coating the nanoparticles with a lipid bilayer, forming plasmonic magnetoliposomes, broadens the spectrum of antitumor drugs (hydrophobic or hydrophilic) that can be loaded and enables their compartmentalization [4].
In this communication, we report novel supramolecular hydrogels based on lysine dehydrodipeptides and address their functionalization with gold-manganese ferrite plasmonic magnetoliposomes (figure 1).
The (micro/nano)structure of the composite gels was evaluated by STEM, Raman and fluorescence spectroscopies and the respective viscoelastic properties were studied by rheology. Ultimately, their relevance as drug delivery platforms and hyperthermia agents was tested.

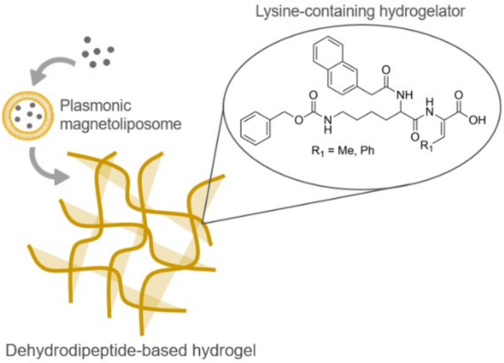

Fig.1. Synthesised dehydropeptide hydrogelators containing magnetic/plasmonic liposomes.

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Self-assembly of bolaamphiphiles based on dehydropeptides

Carolina Amorim[1,*], **Peter J. Jervis, José A. Martins, Paula M.T. Ferreira**

[1]University of Minho, Chemistry Center, 4710-057 Braga, Portugal
**carolinaamorim753@gmail.com*

Self-assembled peptides have emerged as a novel class of biomaterials with various therapeutic applications. Peptide bolaamphiphiles with two polar head groups in both sides of a central hydrophobic core are able to mimic bilayers, self-assembling into many nanostructures. [1]

Recently our research group reported the synthesis, self-assembly and drug delivery assays of of bolaamphiphiles based on dehydropeptides and with an aromatic core (Figure 1). The results showed that some of the new compounds synthesised self-assembled into fibers or vesicles. [2]

In this communication the importance of the structure of the hydrophobic core and of the dehydropeptide on self-assembly will be evaluated and discussed.

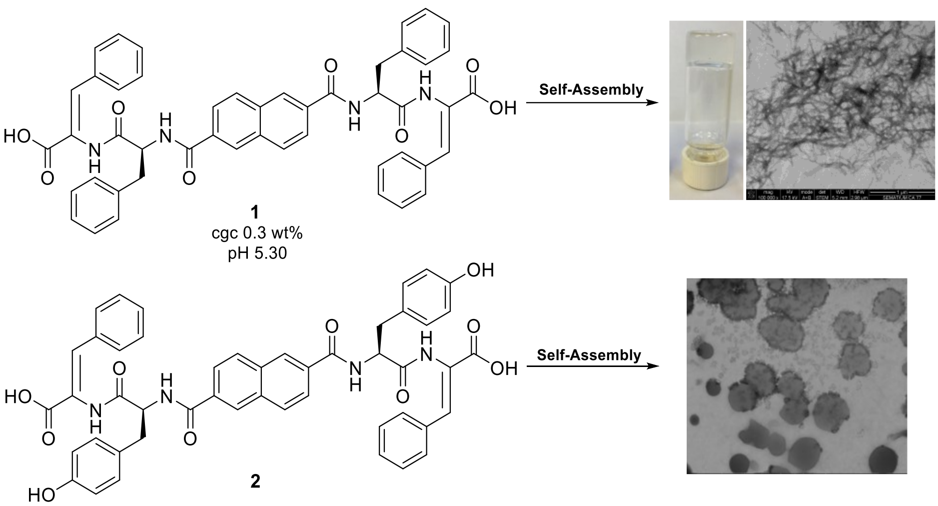

Figure 1. Structures and scanning transmission electron microscopy (STEM) images of bolaamphiphiles **1** and **2**.

Agradecimientos

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Effect of Different Casein Removal Methods on the Purity and Yield of Milk-derived Exosomes

Filipa A. Soares[1,2,*], Salette Reis[1], Cláudia Nunes[1,2]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade Do Porto, Porto, Portugal
[2]ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Porto, Portugal
**up201406128@edu.icbas.up.pt*

Over the last decade, exosomes (Exo) have been showing great potential as nature-derived nanocarriers in drug delivery. From the available source of Exo, bovine milk is the one that provides higher yields and cost-effective processes for their extraction, from higher sample volumes [1]. A variety of methods are being described for the isolation of Exo from milk, but ultracentrifugation remains the gold standard [2, 3]. However, such method alone frequently leads to the co-isolation of protein contaminants, namely casein aggregates [3]. Thus, in this work, we decided to compare the purity and yield of the final exosomal suspensions obtained from bovine milk subjected to different casein removal methods: **(EDTA)** the disassembly of casein micelles by calcium chelation, adding 0.25 M EDTA treatment (1:1; v/v); **(AA)** casein precipitation by acidification adding acetic acid (1:100; v/v); or **(EDTA+AA)** a combination of both. The casein removal steps were included in the beginning of the isolation process, immediately after the skimming step. The pretreatment of the milk samples as well as the centrifugation parameters used after casein removal were optimized and maintained in all the experiments. The obtained exosomal suspensions were characterized by dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), and bicinchoninic acid assay (BCA). Size measurements, obtained by DLS and NTA showed a non-unimodal distribution, characteristic of natural occurring nanovesicles, with mean sizes ranging from 158 to 215 nm, and no significant differences between the four methods. In terms of purity and yield, it is possible to observe, from Table 1 results, that the EDTA-based method is the one that results in higher purity (1.45×10^9 Exo/µg protein), with a yield of 4.11×10^{10} particles/ml of milk. The AA method resulted in higher protein content for lower particle counts comparing to the previous method. EDTA addition combined with acidification promoted the co-precipitation of a high amount of protein aggregates, being this combinatory method not suitable for casein removal. Abrupt changes in pH, caused by sequential addition of EDTA at pH 8.5 and acetic acid may be the underlying reason for this phenomenon. In conclusion, we can say that the efficacy of the casein removal alongside with the chemical nature of the resultant whey must be considered in the design and optimization of milk Exo isolation protocols.

Table 1. Comparison of the mean size, purity (number of particles/μg protein and µg protein/ml milk) and yield (number of particles/ml of milk) of the obtained exosomal suspensions

Method	Mean Size (nm)	Purity		Particle Yield
		μg protein/ml	#particles/µg protein	#particles/ml milk
EDTA	215 ± 5	20 ± 5	1.45E+09	4.11E+10
AA	188 ± 14	54 ± 12	7.50E+08	2.03E+10
EDTA+AA	158 ± 13	414 ± 85	1.19E+09	9.44E+10

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Gold nanoparticles synthesized by natural photosensitizer hypericin

R. Rey-Méndez[1*], N. González-Ballesteros[1], F. Fabbri[2], G. Salviati[3], F. Bigi[3,4], M.C. Rodríguez-Argüelles[1]

[1]CINBIO, Universidade de Vigo, Departamento de Química Inorgánica, 36310 Vigo, Spain
[2]NEST, Istituto Nanoscienze-CNR, Scuola Normale Superiore, 56127 Pisa, Italy
[3]CNR-IMEM, 43124 Parma, Italy
[4]Dipartimento Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, 43124 Parma, Italy
**mcarmen@uvigo.es*

Hypericin (Hyp) is a natural phenantroperylenequinone that can be isolated from plants of the genus *Hypericum* as the leading natural source, but also from insects of the *Coccoidea* family, and the protozoa *Stentor coerulus*. The bioactivities of this molecule are extensive, most of them link to its photosensitivity and its high quantum yield of singlet oxygen and other reactive oxygen species under irradiation with 595 nm light. For example, it was reported that the photosensitivity of Hyp induces cell apopotosis and inhibits the growth of cancer cells making it a excellent antineoplasic agent. It also presents immunomodulatory proporties. Furthermore, has been proven effective against microbial infectious agents, such as against bacteria and against viruses like the herpes virus, bronchitis infection virus, hepatitis C virus or HIV [1]. Finally, it shows interesting antioxidante properties.

However, Hyp presents a highly conjugated planar structure that makes this molecule very hydrophobic and insoluble in aqueous solvents. In physiological conditions, Hyp tends to aggregate by forming dimers, J-aggregated or H-aggregates that cause a great change in the absorption and emission properties of the molecules, affecting its photodynamic behaviour [2]. Therefore, these aggregates do not possess biological activity and they hinder the applications of Hyp in medicine.

For this reason, several strategies has been tested in order to amelliorate its bioavailability and cell selectivity. One of these strategies implicates the use of nanotechnology. The conjugation of Hyp with gold nanoparticles, for instance, can help the photosensitizer better reach the cancer cells and increase its concentration in biological systems by preventing the formation of aggregates. Furthermore, metal nanoparticles have shown the abilities to generate singlet oxygen and are much more stable under irradiation than organic molecules. Therefore, the presence of plasmonic nanoparticles increases the efficiency of conjugated standard photosensitizers.

Following such premises, in this work Hyp was employed to directly reduce $HAuCl_4$ into gold nanoparticles (Au@Hyp). The obtained nanoparticles were fully characterized by UV-Vis spectroscopy, fluorescence spectroscopy, Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM). These technics allow us to confirm the formation of spherical nanoparticles with mean diameter of 17 ± 4 nm and that this conjugation prevents the aggregation of Hyp molecules in aqueous environment. The organic part of these nanoparticles was characterize using techniques such as Nuclear Magnetic Resonance spectroscopy (NMR), Thermogramivetric analysis (TGA) and Fourier Transformed Infrarred spectroscopy (FTIR). Finally, the antioxidant activity of the photosensitizer before and after the synthesis was determined by means of reducing capacity, total phenolic content and DPPH scavenging activity.

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Migration of cellulose nanocrystals from a PLA multilayer film functionalized by Ultrasonic Spray Coater

Antía Lestido-Cardama[1,2*], Miguel Cerqueira[1], Lorenzo Pastrana[1], Ana Isabel Bourbon[1]

[1]INL, International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, Braga, Portugal
[2]Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Pharmacy, University of Santiago de Compostela, Campus Vida, Santiago de Compostela, Spain
**antia.lestido@usc.es*

Food packaging has become an essential tool in food manufacturing since it protects them against contamination (physical, chemical and biological), preserving their nutritional and sensory properties, and extending the product's shelf life. Polylactic acid (PLA) is one of the most attractive bio-based and biodegradable polymers used for food packaging due to its high transparency, good processability, and mechanical properties. However, its use has been limited because of the poor barrier properties, high brittleness, low toughness, slow crystallization rate and low thermal stability. Various strategies have been adopted to improve the properties of biopolymers, such as the addition of nanocoatings creating multilayer systems via a dip-coating or by ultrasonic spray coater, among others.

Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food establishes a Union list of monomers, other starting substances and additives which may be used in the manufacture of plastic materials and articles [1]. Recently, the European Food Safety Authority issued a favourable scientific evaluation for additional substances which should now be added to the current list.

In the present study, coatings of cellulose nanocrystals (CNC) and chitosan were applied on PLA film using the ultrasonic spray coating technique due to the following reasons: process simplicity, precise coating, economical, good transfer efficiency, good reproducibility, and production of droplets in the micrometer range. Physicochemical characterization of the nanoparticles and the film was carried out by combining various techniques such as dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction and microscopy. The migration of CNC applied in the packaging material to food were carried out according to European Normative [1]. Specific migration of CNC from films has been tested by immersion of the side of film with multilayer system in three food simulants (EtOH 10% (v/v), acetic acid 3% (v/v) and isooctane) at 40 °C during 10 days. The quantification was carried out by calcofluor white fluorescence staining and by a colorimetric method for the determination of sugars. Validation parameters, such as linearity, sensitivity, and repeatability for both methods were evaluated.

Microscopy techniques made it possible to visualize the needle-like or rod-like shaped crystalline nanoparticles with lengths that vary from 11.5 ± 0.7 nm to 179.5 ± 35.5 nm according to the DLS measurements. Due to the incorporation of CNC and chitosan, some differences can be observed in the FTIR spectra of the PLA films. The migration results obtained show that there is a small migration of the CNC from the coating ranging from 0.03 mg/L in the case of isooctane to 1 mg/L in the case of 3% acetic acid (v/v).

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Honey2KILL: antimicrobial Portuguese honey towards superbugs

Silva A.[1,2], Pinho S.L.C[1,3,4], Seabra, C.L.[5]*

[1]Coimbra Polytechnic – Escola Superior Agrária de Coimbra, Bencanta, 3045-601 Coimbra, Portugal
[2]CERNAS - Coimbra Polytechnic - ESAC, Bencanta, Portugal
[3]CNC - Center for Neurosciences and Cell Biology, University of Coimbra, 3004-504 Coimbra, Portugal
[4]CIVG - Vasco da Gama Research Center, Vasco da Gama University School, Av. José R. Sousa Fernandes 197 Lordemão, 3020-210 Coimbra, Portugal
[5]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, 4050-313 Porto, Portugal
**cseabra@ff.up.pt*

Honey has been used worldwide for many centuries as a nutrient, an ointment and as medicine. Honey is globally recognized for its antioxidant, anti-inflammatory and antimicrobial bioactivity [1,2] therefore, an attractive alternative treatment for superbug infections. In this sense, the main purpose of this work was to evaluate the physicochemical proprieties of Portuguese and Manuka honey (a well-known New Zealand honey with medical properties) and evaluate its antimicrobial activity. Here, we also report a new bioactive component, honey exosomes (HExs) – vesicle-like nanoparticles obtained from honey. These HEx are membrane-bound nanoscale nanoparticles that contain honey bioactive components, such as lipids, and proteins [3].

The pH determination, colour, protein concentration, total phenolics and methylglyoxal (MGO) characterization were performed. The bacteriostatic and bactericidal activity was tested in *S. aureus, P. aeruginosa* and *K. pneumoniae* by microdilution broth method. The most promising Portuguese honey was used to isolate the HExs. HExs were isolated by serial centrifugation and ultracentrifugation steps and their physicochemical proprieties were assessed in terms of size, surface charge, protein, and total phenolic content.

Our findings showed that Portuguese oak and heather honey presented the most similar physicochemical proprieties to Manuka honey, especially in terms of protein and total phenolic content.

Even though MGO was not detected by UV-VIS spectroscopy in oak and heather Portuguese honey, it still presented bactericidal activity against bacteria tested, but with higher honey concentration when compared to Manuka honey which is rich in MGO [4], suggesting that MGO is not the only factor with antibacterial activity. Homogenous HEx with 130-200 nm of size, and negative surface charge (around -28 mV) were successfully isolated from Portuguese honey, maintaining a higher amount of proteins and total phenolic in their structure.

The findings suggest that honey and exosomes-like vesicles can be a new carrier or adjuvant to counteract superbugs.

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Multiple Lipid Nanoparticles loaded with essential oils as a new approach towards antimicrobial mastitis infection

Martins I.[1,2]**, Pinho S L.C.**[1,3,4]**, Seabra, C.L.**[5*]

[1]Coimbra Polytechnic – Escola Superior Agrária de Coimbra, Bencanta, 3045-601 Coimbra, Portugal
[2]CERNAS - Coimbra Polytechnic - ESAC, Bencanta, Portugal
[3]CNC - Center for Neurosciences and Cell Biology, University of Coimbra, 3004-504 Coimbra, Portugal
[4]CIVG - Vasco da Gama Research Center, Vasco da Gama University School, Av. José R. Sousa Fernandes 197 Lordemão, 3020-210, Coimbra, Portugal
[5]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, 4050-313 Porto, Portugal
**cseabra@ff.up.pt*

Mastitis is an inflammation of the mammary gland in response to infectious agents such as *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Streptococcus agalactiae* which infect the udder and consequently milk production and its quality are affected [1]. Essential oils (EOs) are defined as volatile secondary metabolites of plants that are responsible for smell, flavour, or both. The high level of interest in essential oils is due to their biological properties, which are generally recognized as safe and can also act synergistically with other compounds, allowing them to be used as bioactive compounds, including against pathogenic bacteria [2,3]. Although the effective effect of essential oils against bacteria, some drawbacks are needed to be overcome. This work aims to load essential oils, namely lavender, clove and oregano on a biodegradable and biocompatible lipid-based drug delivery system- multiple lipid nanoparticles (MLNs) to improve their antimicrobial activity to fight *S. aureus*, *S. epidermidis* and *P. aeruginosa* and to prevent mastitis development and udder infection.

MLNs production was based on a hot homogenization method combined with ultrasonication [4]. The MLNs produced exhibited a mean hydrodynamic size below 300 nm, and negative surface charge of around -30 mV and high encapsulation efficiency of around 90%. MLNs were stable under storage conditions for at least 4 weeks. MLNs has bacteriostatic activity against *Staphylococcus* spp., in a dose-dependent manner. Hemocompatibility studies revealed that MLNs exhibited a low hemolytic activity for concentrations below 0.312% of EOs-MLNs.

Our findings suggest that EOs-MLNs may be used as an antibacterial nanotherapeutic or an adjuvant or prophylactic agent to prevent the development of mastitis.

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Naringin nano-delivery systems for inflammatory conditions

Andreia Marinho[1,2,*], Catarina Leal Seabra[1], Sofia A. Costa Lima[1], Salette Reis[1] and Cláudia Nunes [1]

[1]LAQV, REQUIMTE, Faculdade de Farmácia, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal
[2]LAQV, REQUIMTE, Faculdade de Ciências, Universidade do Porto, R. Campo Alegre s/n, 4169-007 Porto, Portugal
**up2021205710@edu.fc.up.pt*

Naringin, the main flavonoid found in grapefruit, has a wide spectrum of beneficial health effects, including its anti-inflammatory activity [1]. In addition, recent studies report that naringin has a protective effect on joint destruction (models of rheumatoid arthritis) [2] and is effective in protecting against bone diseases (such as osteoporosis) [3]. Despite presenting itself as a therapeutic promise, naringin sees its application in the clinic as limited, due to the extensive metabolism of phases I and II that it undergoes in the liver and its decomposition by the intestinal flora, which makes it have a low bioavailability after oral admission. To overcome these challenges, in recent years nanotechnology has assumed an emerging role. Nanoparticle-based drug delivery systems make it possible to protect the compounds of interest against degradation, improve their solubility and prolong their circulation time. Also noteworthy is the possibility of surface functionalization based on specific markers of the pathology of interest, which leads to the delivery of the therapeutic compounds to target sites.

In this sense, lipid nanoparticles were developed for the targeted delivery of naringin in the joint. As a way of directing the NPs to the CD44 receptor, which is overexpressed by activated macrophages [3], functionalization with hyaluronic acid was performed. Nanoparticles were characterized in terms of hydrodynamic diameter, polydispersity index, zeta potential, and encapsulation efficiency. *In vitro* studies show controlled release of naringin along the gastrointestinal tract and good biocompatibility (THP-1 cell line). It was also shown that the developed nanoparticles still can regulate inflammatory mediators.

Acknowledgments

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The role of chemical modified SiO_2 nanoparticles in the tribological performance of a paraffinic oil

<u>María J.G. Guimarey[1,2*]</u>, José M. Liñeira del Río[1,3], Fátima Mariño[1], Arturo Castro Currás[1], Vanesa Somoza[1], M.J.P. Comuñas[1], Josefa Fernández[1]

[1]Laboratory of Thermophysical and Tribological Properties, Nafomat Group, Department of Applied Physics, Faculty of Physics and Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain
[2]Department of Design and Engineering, Faculty of Science & Technology, Bournemouth University, Talbot Campus, Poole BH12 5BB, United Kingdom
[3]Unidade de tribologia, vibraçoes e manutençao industrial, INEGI, Universidade do Porto, Porto, Portugal
*<u>*mariajesus.guimarey@usc.es*</u>

Nanolubricants emerged as a new class of lubricants formulated from base oil and dispersed nanoparticles (NPs). Nevertheless, the bottleneck for further nanolubricant development is aggregation and sedimentation of the NPs [1]. A stable suspension of NPs is essential for a potential lubricant, being a possible solution the chemical modification of NPs surface [2]. In this work, the tribological properties of SiO_2 nanoparticles, both uncoated and coated with stearic acid (SiO_2-SA), as additives of a low viscosity paraffinic oil at different concentrations (0.15, 0.30, 0.45, 0.60 wt%) are analyzed. An esterification reaction was used to functionalize the SiO_2 NPs with stearic acid following a procedure similar to that used previously by Mariño et al. [3]. Tribological experiments were performed at 393.15 K with all the studied nanolubricants. All the nanolubricants containing SiO_2-SA NPs improve the anti-friction capabilities of the base oil, with the optimum concentration being 0.60 wt%. The best anti-wear results were also achieved with the 0.60 wt% SiO_2-SA NPs nanolubricant with reductions of 21%, 22% and 54%, in wear scar diameter, wear track depth and worn area, respectively. Furthermore, Raman mapping on wear scars (Fig. 1) has revealed that the tribological mechanisms of NPs are tribofilm formation and mending.

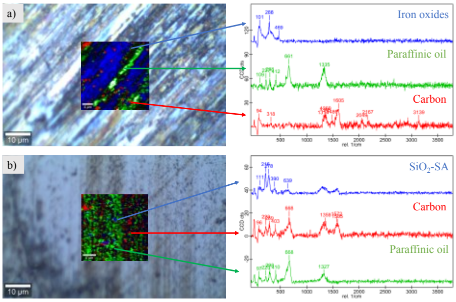

Fig. 1. Raman mapping of worn tracks lubricated with a) neat paraffinic oil and b) 0.60 wt% SiO_2-SA nanolubricant.

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Development of a Fluorescent Nanostructured Lipid Carrier (NLC) by a High-energy method

Jesus, J[1,2]*, Seabra, C.L.[3], Pinho, S.L.C[1,4,5]*

[1] Coimbra Polytechnic – Escola Superior Agrária de Coimbra, Bencanta, 3045-601 Coimbra, Portugal [2] CERNAS - Coimbra Polytechnic - ESAC, Bencanta, Portugal
[3] LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, 4050-313 Porto, Portugal
[4] CNC - Center for Neurosciences and Cell Biology, University of Coimbra, 3004-504 Coimbra, Portugal
[5] CIVG - Vasco da Gama Research Center, Vasco da Gama University School, Av. José R. Sousa Fernandes 197 Lordemão, 3020-210 Coimbra, Portugal
**sonia.pinho@esac.pt*

Nanotechnology has a huge impact on the pharmaceutical, biotechnology, food, and cosmetics industries. Most of the approved drugs are lipophilic and have poor solubility [1]. Lipid nanocarriers have a huge potential for enhancing the physicochemical characteristics and behaviour of poorly water-soluble drugs, such as aqueous dispersibility and oral bioavailability.[2]

This investigation presents a novel nanostructured lipid carrier (NLC) based on a mixture of solid lipid glyceryl palmitostearate (Precirol® ATO 5), an oil composed of a chemically modified fluorescent oleic acid and a surfactant base on a polysorbate 20 (Tween® 20). These NLCs were developed by a simple hot homogenization and sonication method and yielded different NLCs with different amounts of fluorescent liquid lipid with narrow size distribution. The novel NLCs were characterized by dynamic light scattering (DLS), zeta potential, nanoparticle tracking analysis (NTA), and colloidal stability. The fluorescent content was determined by UV-VIS spectroscopy. The cytotoxicity of the different nanostructured lipid carriers with different percentages of fluorescent liquid lipid was evaluated by resazurin assay. Finally, to elucidate the mechanism of the formation of the NLC several molecular dynamics simulations were conducted.

Our results suggest the potential of novel NLC as a drug delivery system for poorly water-soluble drugs.

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New supramolecular hypergelators based on dehydroamino acid residues for biomedical applications

Carlos B.P. Oliveira[a], Loic Hillou[b], Peter J. Jervis[a], Paula M. Ferreira[a], José A. Martins[a]

[a]Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

[b]Institute for Polymers and Composites/13N, Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

Employing amino acids and peptides as the molecular building blocks of hydrogelators provides unique opportunities for generating supramolecular hydrogels, owing to their inherent biological origin, bioactivity, biocompatibility, and biodegradability [1]. Ultrashort peptides (<8 amino acids) attached to an aromatic capping group are particularly attractive alternatives as minimalistic LMW hydrogelators [2].

Peptides of low critical gelation concentration (CGC) are especially desirable due to the low amounts required to obtain a hydrogel, which makes them more cost-effective and more biocompatible in cases where the monomeric hydrogelator is cytotoxic.

With the aim of developing novel hypergelators, we targeted a set of new peptides based on non-natural amino acids. Inspired by the dipeptide developed by Gazit`s group, which is the gelator with the lowest CGC (0.002 wt%) ever reported [3] (**Figure 1A**), two novel hydrogelators were designed (**Figure 1B**). They were then studied for their mechanical properties and injectability.

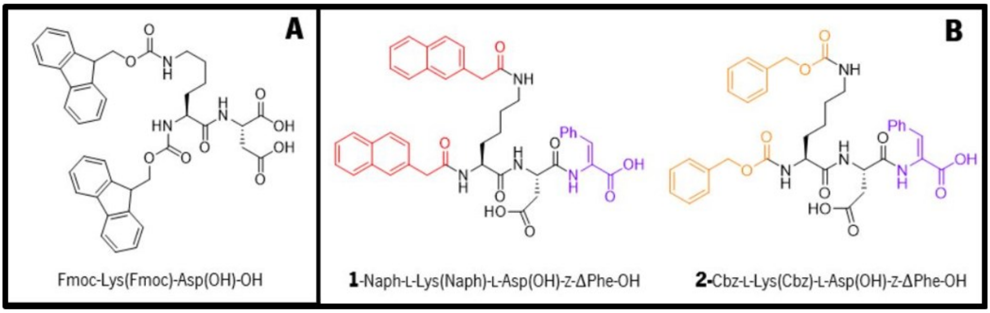

Fig.1. (A) Structure of the hypergelator developed and studied by Gazit`s group. (B) Structure of the hypergelators synthetized and studied for their hydrogelation ability.

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Nanoplatforms drive slow down in skin ageing

Renata Basto[1], Zinaida Shakel[1], Aikaterini Spanou[1], Ana Isabel Barbosa[1], Cláudia Nunes[1], Sofia A Costa Lima[1,2,]* and Salette Reis[1]

[1]LAQV, REQUIMTE, Faculty of Pharmacy, University of Porto, Portugal.
[2]LAQV, REQUIMTE, ICBAS, University of Porto, Portugal.
Email: slima@icbas.up.pt

Skin ageing is induced by both intrinsic and extrinsic factors, namely solar ultraviolet (UV) radiation. The current increased levels of UV radiation provoke early skin ageing, which in turn impairs the protective ability of the skin and leads to various diseases, including skin cancer. Biological mechanisms of skin ageing involve the action of reactive oxygen species, genetic mutations, as well as hormonal changes.

Genistein belongs to the large group of biologically active polyphenolic compounds while niacinamide is an amide form of vitamin B3, and both exhibit remarkable anti-ageing properties. Yet, their physicochemical properties difficult an effective skin delivery *per se*. Here different smart delivery systems were designed and evaluated to improve genistein and niacinamide skin delivery. For genistein, topical delivery made from freeze-dried softisan-based lipid nanoparticles was developed with storage stability at room temperature at least up to 12 weeks. The antioxidant activity is maintained in genistein-loaded nanoparticles, with a protective effect when compared to the same amount of free compound. Cellular biocompatibility towards keratinocytes was confirmed up to 2 mg/mL in lipid, corresponding to 100 µg/mL of entrapped genistein. Upon freeze-drying, the nanoformulation formed an oleogel with rheological properties suitable for skin application. For niacinamide skin delivery a hybrid nanogel was designed using k-carrageenan and poly-vinylpyrrolidone polymers combined with jojoba oil, as a permeation enhancer. Transethosomes were prepared by the thin-film hydration method to allow a niacinamide-controlled delivery. The hybrid hydrogels exhibited robust, porous, and highly aligned macrostructures, and when present, jojoba oil changed their morphology. Skin permeation studies with transethosomes-loaded hydrogels showed that nanogels per se exhibit a more controlled and enhanced permeation, in particular, when jojoba oil was present in the transethosomes. These promising nanogels protected the Human keratinocytes from UV radiation and thus, can be added to sunscreens or after-sun lotions to improve skin protection.

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Nanolubricants stability: surface modification of nanoparticles

José M. Liñeira del Río[1,2*], María J.G. Guimarey[1,3], Fátima Mariño[1], María J.P. Comuñas[1],
Enriqueta R. López[1], Josefa Fernández[1]

[1]Laboratory of Thermophysical and Tribological Properties, Nafomat Group, Department of Applied Physics, Faculty of Physics and Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, España
[2]Unidade de tribologia, vibraçoes e manutençao industrial, INEGI, Universidade do Porto, Porto, Portugal
[3]Department of Design and Engineering, Faculty of Science & Technology, Bournemouth University, Talbot Campus, Poole BH12 5BB, United Kingdom
*josemanuel.lineira@usc.es

The formulation of stable lubricants with nanoadditives (nanolubricants) presents a huge challenge due to the nanoparticles tendency to aggregate, and then settle down, due to Van der Waals forces. To address this issue, different methods have been tested to improve the nanolubricants stability, such as physical treatments, the use of surfactants and surface modification of nanoparticles [1]. Regarding the last method, our group has used different agents to modify the surface of nanoadditives, obtaining nanolubricants with promising stabilities [2,3]. In this work we review different chemical modifications performed and we compare the stability times achieved for nanolubricants based on synthetic and vegetable oils. Table 1 summarises the main surface modification agents used to functionalize nanoparticles with different morphologies and sizes, the base oils used to prepare the nanolubricants and the stabilities achieved since their preparation. The stability of nanolubricants was analysed by visual control and by refractometry techniques.

Table 1. Stabilities of nanolubricants prepared with different surface modification agents of nanoparticles.

Nanoparticles	Surface modification	Base Oil	Temporal stability (days)
Fe_3O_4 (6.3 nm)	Oleic acid (OA)	Trimethylolpropane trioleate	330
rGO	Octadecylamine (ODA)	Synthetic biodegradable and polymeric ester	28
SiO_2 (8 nm)	Stearic acid (SA)	Polyalphaolefin PAO6	80

The functionalization of the nanomaterials has been carried out by means of different surface modification methods, such as a modification of Sun's method [4]. The obtained results revealed that the nanolubricants formulated with Fe_3O_4 (6.3 nm) magnetic nanoparticles functionalized with oleic acid have been stable for more than 11 months.

Acknowledgments

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Enhanced antioxidant activity of silver nanoparticles synthesized by *Codium tomentosum* aqueous extract

N. González Ballesteros[1], R. Rey Mendez[1,*], M. Lastra-Valdor[2], A. Cavazza[3], F. Bigi[3,4], M. C. Rodríguez Argüelles[1]

[1]CINBIO, Universidade de Vigo, Departamento de Química Inorgánica, 36310 Vigo, España
[2]Centro de Investigación Marina, Universidade de Vigo, 36331 Vigo, España
[3]Dipartimento Scienze Chimiche, della Vita e della Sostenibilità Ambientale. Università di Parma, 43124 Parma, Italia.
[4]IMEM Parma-CNR, 43124 Parma, Italia
**raquel.rey.mendez@uvigo.es*

The outstanding physico-chemical properties of silver nanoparticles, such as high surface per volume ratio, conductivity, ability to interact with light thanks to the plasmonic resonance, and biocompatibility have made them suitable for applications in a wide number of fields such as photoelectronic, bio-sensing and catalysis. Remarkably, the most well-known application of silver nanoparticles is in the medical sector, thanks to their broad-spectrum antimicrobial activity [1].

Despite their potential, the applicability of this type of nanoparticles is clearly affected by the method of synthesis. Especially when producing nanoparticles for the food and therapeutic industries the use of toxic reagents must be avoided. The implementation of new synthetic methods to produce uniform nanoparticles in a sustainable, eco-friendly, and cost-effective way is needed. In this regard, the biological methods of synthesis have been developing as a powerful alternative to the traditional chemical and physical methods. In this approach, expensive and toxic reagents and solvents are substituted by biomass or natural extracts as a source of reducing agents [2]. Among the different organisms available, we have focussed our attention on algae, a diverse group of organisms rich in antioxidants and bioactive molecules. Specifically, in this work we present the results obtained for the synthesis of silver nanoparticles led by *Codium tomentosum* (CT).

C. tomentosum is a green macroalgae native to the North East Atlantic Ocean, found on exposed shores in deep rock pools, and in the lower intertidal and subtidal zone. This specie has drawn attention because of its anticoagulant, anti-inflammatory, antioxidant and chemotherapeutic activity [3]. In this work, CT extract has been employed for the preparation of an aqueous extract to be used as the reducing agent on the synthesis of silver nanoparticles. The Obtained nanoparticles were fully characterized by UV-Vis spectroscopy, Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM); These technics allowed us to confirm the formation of spherical nanoparticles with mean diameter of 20.3±5.5. Moreover, Fourier transform infrared spectra (FTIR) of CT extract and Ag@CT were recorded to identify the functional groups of biomolecules that could be involved in the formation and stabilization of the nanoparticles. Finally, the antioxidant activity of the extract before and after the synthesis, were determined by means of the analysis of the reducing activity, total phenolic compounds and DPPH scavenging activity.

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QUÍMICA ANALÍTICA

Polycyclic Aromatic Hydrocarbons Determination in Human Adipose Tissue

Sara Sousa[1,2,3,*], Paula Paíga[1], Maria João Ramalhosa[1], Diogo Pestana[2,4], Gil Faria[2,5], Conceição Calhau[2,4], Cristina Delerue-Matos[1], Valentina Fernandes Domingues[1]

[1]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, 4200-072 Porto, Portugal
[2]Center for Research in Health Technologies and Information Systems, 4200-450 Porto, Portugal
[3]Departamento de Química, Faculdade de Ciências, Universidade do Porto, rua do Campo Alegre s/n, 4169– 007 Porto, Portugal
[4]Nutrição e Metabolismo NOVA Medical School Faculdade de Ciências Médicas Universidade Nova de Lisboa, 1169-056 Lisboa, Portugal
[5]General Surgery Department, S. João Hospital, Faculty of Medicine, University of Porto, 4200-319 Porto, Portugal
**sara_sousa_23@hotmail.com*

Polycyclic Aromatic Hydrocarbons (PAHs) are environmental persistent organic pollutants formed during incomplete combustion and pyrolysis processes. Sixteen PAHs has been classified as possible carcinogens and priority pollutants by International Agency for Research on Cancer and the European Commission. Humans are continuously exposed to PAHs, mostly through ingestion or by inhalation and dermal contact. Severe health effects as diabetes, oxidative stress, inflammation, cancer, infertility, poor foetal development, cardiovascular disease, amongst others are associated with PAHs exposure. PAHs are lipophilic compounds as such tend to accumulate in adipose tissue, however only few analytical methods are developed using this matrix, especially for PAHs assessment. Even though, adipose tissue is the ideal matrix to assess over time accumulation of lipophilic pollutants. Hence, the present study aimed to reduce the existent gap in working with this highly fat and complex matrix [1].

The present work intended to develop a method for the extraction and quantification of PAHs in adipose tissue using an ultrasound-assisted extraction (UAE) and HPLC. This methodology allowed the extraction of these pollutants from adipose tissue while keeping up with the increasing demand of greener methodology. UAE was performed as described in the authors previously study for other lipophilic compounds in the same matrix [2]. Briefly, 0.4 g of adipose tissue was homogenized with *n*-hexane in an ultrasonic processor. After which, *n*-hexane was dried under nitrogen flow and exchange by other solvent in order to reduce the amount of fat and other interferents prior to PAHs analysis. Different solvents or mixtures of solvents were tested, namely with chloroform, toluene, dichloromethane, acetone, ethyl acetate, propanol, ethanol, methanol and acetonitrile. PAHs were quantified in a Shimadzu LC system equipped with photodiode array (PAD) and fluorescence (FLD) detectors inline. PAHs were separated in a CC 150/4 Nucleosil 100-5 C18 PAH column [3]. The selected method was validated for linearity, method detection limits (MDLs), method quantification limits (MQLs), precision (intra- and inter-day), recovery, matrix effect (ME) and in human adipose tissue samples from women undergoing bariatric surgery at Hospital de São João, Portugal (protocol approved by the Ethics Committee of Hospital São João, CE 146-09).

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QA28

APLICACIONES DE LA MICROSCOPÍA RAMAN CONFOCAL

Vázquez Fernández E[1*], López Rodríguez, J[1], Muras González J[1], Costa Pombo N

[1]Unidade de Espectroscopía IR-Raman
Rede de Infraestructuras de Apoio á investigación e ao Desenvolvemento Tecnolóxico (RIAIDT)
Universidade de Santiago de Compostela-Edificio CACTUS, Campus Vida (España)
ezequiel.vazquez@usc.es

La espectroscopía raman junto con la infrarroja conforman la espectroscopía vibracional. En los últimos años el desarrollo de láseres de estado sólido, detectores más sensibles, eficientes y rápidos, unido al desarrollo de la microscopía confocal, permiten desarrollar equipos raman confocales capaces de ser utilizados en numerosos campos científicos. La mínima o nula preparación requerida de las muestras es otra baza que juega a favor de la Microscopía Raman Confocal [1].

En esta comunicación queremos mostrar una pequeña parte de las aplicaciones que tiene esta técnica analítica y que fueron realizadas en la Unidad de Espectroscopía IR-Raman de la USC. Entre ellas podemos destacar:

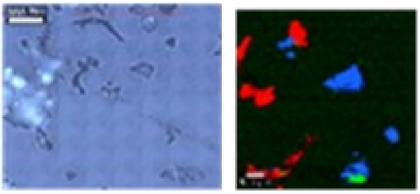
a)Microplásticos: La espectroscopía raman confocal permite la identificación de microplásticos<20 micras y es una técnica de mayor rapidez y resolución que la espectroscopía infrarroja.

b)Tejidos Biológicos: Las células vivas previamente fijadas sobre soporte de CaF2 pueden ser analizadas por microscopía raman confocal para ver penetración de medicamentos, etc…

c)Industria Farmacéutica: El poder determinar la composición, distribución, tamaño, etc… de principios activos y excipientes en las distintas presentaciones de los medicamentos de una forma rápida y fiable es otro de los puntos fuertes de la microscopía raman confocal.

d) SERS (Surface Enhanced Raman Scattering): La dispersión raman es muy débil. En determinados casos es necesario un aumento de señal. A través de la utilización de nanopartículas y/o sustratos, generalmente de Au/Ag, se puede aumentar de forma considerable esa señal para poder estudiar áreas de interés en las muestras.

a)



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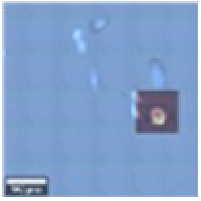

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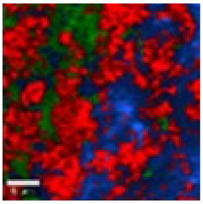

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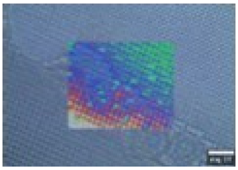

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Paper-based analytical devices for instrumental and smartphone-based fluorimetric sensing of environmentally relevant inorganic species

Lorena Placer[*], **Isela Lavilla, Francisco Pena-Pereira, Carlos Bendicho**

Centro de Investigación Mariña, Universidade de Vigo, Departamento de Química Analítica e Alimentaria, Grupo QA2, Edificio CC Experimentais, Campus de Vigo, As Lagoas, Marcosende, 36310 Vigo, Spain
**lorena.placer.vidal@uvigo.es*

Luminescent molecules derived from citric acid (CA) are receiving increasing attention in the recent years. Their natural origin, green and straightforward synthesis and excellent photoluminescence properties make them highly promising for luminescence-based sensing purposes [1,2].

This work reports on the synthesis, characterization and application of two luminescent probes prepared via one-pot reaction of CA and two β-aminothiols, namely L-cysteine (Cys) and cysteamine. These luminescent probes were used for ammonia, bromide and bromate sensing.

Both CA-based fluorophores showed pH-dependent dual excitation/dual emission profile at acidic and alkaline pH values. The fluorescence intensity ratio obtained at specific excitation/emission wavelength pairs, namely 348/408 nm and 384/444 nm, showed a sigmoidal relationship with pH that hold great promise for pH sensing studies. An analogous relationship was observed with both fluorophores when B and G colour channels were selected for smartphone-based pH sensing. In preliminary studies, it was also observed that Br_2 produced a quenching of fluorophores luminescence. In view of the observed effects, the development of enrichment/sensing strategies involving both fluorophores was considered for the determination of species of environmental interest such as NH_4^+, Br^- and BrO_3^-.

Paper-based analytical devices (PADs) modified with both fluorophores were implemented in headspace (HS) microextraction systems for the selective and sensitive fluorimetric determination of environmentally relevant ions. Thus, HS-PADs were conveniently combined with solid-state fluorimetry and smartphone-based fluorimetry for the determination of ammonia [3] and Br^- and BrO_3^- [4], respectively. Under optimal conditions, the methods showed repeatabilities in the range of 5.8-8.3% and limits of detection of 37 µM, 0.07 µM and 0.007 µM for ammonia-N, Br^- and BrO_3^-, respectively. The reported methods yielded recoveries in the range of 85-106% when applied to the analysis of liquid and solid environmental samples.

Acknowledgment
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Development of a novel cost-effective method for the density separation of microplastics from marine sediments, followed by quantitative ^{1}H-nuclear magnetic resonance spectroscopy determination

Javier López-Vázquez[1*], **Rosa Montes**[1], **Víctor M. Sánchez-Pedregal**[2], **José Benito Quintana**[1], **Rosario Rodil**[1]

[1]Department of Analytical Chemistry, Institute of Research on Chemical and Biological Analysis (IAQBUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Galicia, Spain.
[2]Department of Organic Chemistry, School of Chemistry, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Galicia, Spain.
*j.lopez.vazquez@usc.es

Microplastics (MPs), defined as plastic particles smaller than 5 mm, are considered a new class of persistent environmental pollutants of global concern. They may reach the environment directly from manufactured products that contain MPs (e.g. some personal care products), i.e. primary MPs, or be formed in the environment due to degradation, transformation, and deterioration of parent (micro)plastics driven by photo-oxidation and physical processes, i.e. secondary MPs [1]. MPs have been found in almost every compartment affected by human interaction, but have been of particular concern in the marine environment, as a major sink of those pollutants [2].

Once MPs reach the marine environment, they can be hazardous for marine organisms, including phytoplankton, zooplankton, bivalves (e.g. mussels), marine mammals, seabirds and fish. They can not only cause physical damage to marine organisms due to contact, absorption or ingestion, but also become a potential pathway of exposure to organic pollutants for marine organisms [1,3]. Furthermore, MPs can then enter the human food chain eventually threatening human health, for example through the ingestion of seafood.

The determination of MPs in the marine environment, and particularly sediments and sand, is very laborious. Furthermore, separation of MPs from other particles is typically conducted in large density separators. Consequently, the development of reliable, simpler and cost-effective analytical methods is necessary in order to better assess their distribution in the marine environment.

Therefore, the aim of this study was to develop a method for the separation, identification, and quantification of plastic particles from aquatic sediments. With that purpose, a density separation using a novel small-scale separation setup made of glass was developed. Thus, it was tested for the separation of spiked sediments (100 g) with 1.6 g/cm^3 zinc chloride with different MPs (polyethylene, polystyrene, polypropylene, polyvinyl chloride and polyethylene terephthalate) at two environmentally realistic concentration levels (2 and 20 mg). The trueness of the method was calculated by a gravimetric method and quantitative ^{1}H-NMR spectroscopy (qNMR) for polyethylene terephthalate, polyvinyl chloride and low-density polyethylene, producing recoveries higher than 81% in all cases. Moreover, the combination with qNMR led to limits of quantification below 0.01 ng/g. Finally, the developed method was applied to a few samples of beach sediments from different sites of the Galician coast (Norwest of Spain) with concentrations of polyethylene terephthalate and low-density polyethylene ranging from 62 to 186 ng/g and 82 to 100 ng/g, respectively.

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Determination of Sulfide in Waters by Smartphone-Based In-Drop Colorimetric Plasmonic Sensing involving hydrophobized PADs

N. Villarino*, **F. Pena-Pereira, I. Lavilla, C. Bendicho**

Centro de Investigación Mariña, Universidade de Vigo, Departamento de Química Analítica e Alimentaria, Grupo QA2, Edificio CC. Experimentais, Campus de Vigo, As Lagoas, Marcosende, 36310, Vigo, Spain
**nevillarino@alumnos.uvigo.es*

Plasmonic nanoparticles (NPs) are receiving increasing interest due to their unique properties. Particularly, plasmonic NPs show outstanding potential for the determination of target analytes on the basis of their interaction/reaction with subsequent modification of the optical properties of NPs. Apart from miniaturized optical detection systems [1], plasmonic NPs are being used in combination with nonconventional detection devices such as digital cameras and smartphones, which are becoming relevant to carry out on-site analysis, especially in combination with paper based analytical devices (PADs) [2]. However, methods involving NPs usually show limitations associated to the lack of sensitivity and selectivity that can hinder their application to the analysis of real samples. The implementation of hydrophilic cellulose substrates modified with NPs in headspace approaches can overcome the above mentioned limitations, even though the retention of NPs in paper is a requirement under this configuration, and a relatively large amount of NPs could be required.

With the aim to develop a sensitive, portable and straightforward method for sulfide determination in waters, we evaluated in this work the applicability of different waterproof cellulose-based substrates, namely Whatman 1PS, polyethylene-coated filter paper and tracing paper, as holders of plasmonic NPs to carry out both the headspace microextraction process and subsequent colorimetric determination [3]. The approach was based on the color change of the colloidal microdrop when exposed to *in situ* generated H_2S with smartphone-based detection. Whatman 1PS was selected as the substrate of choice, showing remarkable compatibility with the NPs. Remarkably, the waterproof substrate enabled hanging relatively large drop volumes (20 µL) during microextraction, while maintaining the spherical shape of the drop for smartphone-based detection.

Under optimal conditions, the method yielded a limit of detection of 0.46 µM for sulfide, and a repeatability of 4.4% (N=8), expressed as relative standard deviation. The applicability of the method developed herein was demonstrated by the analysis of environmental waters, showing recoveries in the range of 91-107%.

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Occurrence and persistence of fungicides and insecticides in vineyard soils

V. Fernández-Fernández[1*], A. Díaz[1], L. Pérez-Mayán[1], S. Triñanes[1], T. Arias[1], R. Montes[1], M. Ramil[1], P. Blanco[2], I. Rodríguez[1]

[1]Department of Analytical Chemistry, Nutrition and Food Science. Research Institute for Chemical and Biological Analysis (IAQBUS), University of Santiago de Compostela, Santiago 15782, SPAIN
[2]Estación de Viticultura e Enoloxía de Galicia (EVEGA-AGACAL), Ponte San Clodio, Leiro 32428, SPAIN
**e-mail: victoriafernandez.fernandez@usc.es*

Synthetic pesticides, and particularly fungicides, have permitted to increase significantly the productivity of vineyards located in geographic regions with a high incidence of pests. Systemic compounds are particularly effective. These pesticides have the ability to penetrate and to travel inside plant tissues, offering higher protection against pests than contact compounds. Furthermore, their activity is less dependent of climate conditions, such as rain events and showers after application. In addition to plant leaves and fruits, soil is the main receptor of pesticides used in viticulture. Thus, it is important to understand the presence, the persistence, and the further interaction of these compounds with the soil matrix, including the evaluation of their migration risk.

In this presentation, a multianalyte LC-ESI-MS/MS method, following compounds extraction by pressurized liquid extraction (PLE), is applied to determine the residues of a group of 50 pesticides (fungicides and insecticides) in soils from vineyards located in two different wine producing areas (Ribeira Sacra and Ribeiro) in Galicia. The evaluated soils presented different features as regards pH, organic content and texture [1]. The study considers the occurrence of compounds in samples obtained in different dates after application, at two different depths (topsoil: 0-5 cm, and 5-20 cm layer), in order to assess the dissipation rate and the migration profile of the compounds in this compartment. Furthermore, the enantiomeric fractions (EFs) of a selection of chiral compounds are determined in some of the samples (1) to identify their use either as racemates or as active enantiomer, and (2) to detect the potential existence of enantioselective degradation/ migration processes in the soil compartment.

Application of the method to vineyard soil samples reflected that, a group of 10-12 compounds presented a high frequency of detection, with concentrations ranging from 10 to more than 1000 ng g^{-1} in the topsoil layer (0-5 cm). In general, residues in the layer from 5 cm to 20 cm were significantly lower; however, whilst pesticide levels in topsoil decreased during rest of vines (winter time), those in the layer from 5 to 20 cm increased for some of detected species. Enantiomeric analysis of chiral compounds reflected their systematic application as racemates with the exception of the fungicide metalaxyl, which showed variable enantiomeric fractions in the processed samples. In some cases, only the non-active enantiomer (not commercially available) was quantified, pointing out to an enantioselective degradation mechanism for this fungicide in some vineyards.

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GC-MS screening method for the identification of semi-volatile compounds in bio-based and biodegradable food packaging materials

P. Vázquez Loureiro[1*], R. Sendón[1], L. Barbosa-Pereira[1], J. Bustos[2], P. Paseiro-Losada[1], A. Rodríguez-Bernaldo de Quirós[1]

[1]Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Pharmacy, University of Santiago de Compostela, 15782, Santiago de Compostela, Spain
[2]National Food Center, Spanish Agency of Food Safety and Nutrition, E-28220 Majadahonda, Spain
* *patriciavazquez.loureiro@usc.es*

Bio-based and biodegradable plastics are being used for food packaging applications as an alternative to conventional plastics derived from petroleum feedstocks due to the environmental pollution originated by the use of traditional petroleum-based non- biodegradable polymers [1, 2].

Bio-based polymers like other food contact materials may transfer low molecular weight constituents into the food and therefore represent a risk for the consumers' health. However, the chemical safety of these sustainable materials has been scarcely studied [1].

In the present work, a Gas Chromatography coupled to Mass Spectrometry (GC-MS) screening method for the identification of semi-volatile components in bio-based and biodegradable food packaging materials was developed. Six different plastic materials labeled as biodegradable, bio-based or compostable were collected to carried out the study. The samples, including bags for foodstuff and films were provided by the industry and acquired from retailers. In developing the extraction method, two solvents, i.e., methanol and acetonitrile at 70ºC for 24 h were tested. The best results in terms of the number of extracted compounds was obtained with methanol.

The chromatographic conditions used were the following: the carrier gas used was He using a flow of 1 mL/min. The extracts were analysed by GC-MS using Electron Ionization (EI) in full scan mode (35-500 m/z). The separation of the compounds was made using a Rxi-5SilMS (30 m x 0.25 mm, 0.25 µm) column as stationary phase. The oven ramp temperature was from 40 to 300 ºC and the transfer line and detector temperatures were 300 ºC.

The method has proved useful for the determination of low molecular weight compounds, which can potentially migrate into the food. A wide variety of compounds including 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, Tributyl acetylcitrate (ATBC), Diethyl phthalate (DEP), 9-octadecenamide among others were identified. The identification of the different compounds was obtained by comparison with spectral libraries such as NIST/EPA/NIH 2020 and Wiley RegistryTM 12th edition. It is also interesting to highlight that some compounds detected (e.g., benzophenone, 9-octadecenamide, 13-docosenamide) exhibited high toxicity (Class III) according to Cramer rules.

The proposed method allowed the rapid identification of potential semi-volatile migrants in the bio-based packaging materials. It could be used as a screening tool for the selection of relevant substances the migration of which should further be studied in specific migration tests.

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Composição fenólica e atividade biológica de extratos de casca e ramos de *Juniperus communis* L. (zimbro comum)

Virginie Xavier[1,2], Tiane C. Finimundy[1,2], Joana S. Amaral[1,2], José Pinela[1,2], Ricardo C. Calhelha[1,2], Izamara de Oliveira[1,2], Irene Mediavilla[3], Luis Saúl Esteban[3], Isabel C.F.R. Ferreira[1,2], Sandrina A. Heleno[1,2], Lillian Barros[1,2]*

[1]Centro de Investigação Montanha (CIMO), Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal
[3]CEDER-CIEMAT, Autovia de Navarra A-15, Salida 56, 42290 Lubia, Spain
**lillian@ipb.pt*

A espécie *Juniperus communis* L., comumente designada "zimbro" em Portugal, é uma conífera, pertencente à familia Cupressaceae e adaptada à baixa disponibilidade de nutrientes no solo.

O zimbro foi usado na medicina tradicional para tratar infeções urinárias, dermatites ou como diurético, entre outros, dada a sua composição em bioativos como compostos fenólicos, terpenóides e ácidos orgânicos. Nos últimos anos, vários estudos reportam o seu potencial antimicrobiano, antioxidante, anti-inflamatório, efeitos anti-diabéticos, hipocolesterolémicos e ainda a sua ação neuroprotetora, bem como capacidade antiproliferativa contra células cancerígenas e a capacidade de ativar mecanismos hepatorrenais e gastroprotetores [1,2].

No âmbito do presente trabalho, que surge no contexto do projeto BBI-JU BeonNAT, a casca do zimbro foi separada da parte aérea e posteriormente moída à parte da restante biomassa (parte aérea composta por ramos e agulhas) para comparar estas duas frações ao mesmo tempo que se pretende aproveitar todas as partes da planta, promovendo um conceito de economia circular.

Depois de moídas, as amostras foram extraídas por maceração e a composição fenólica de cada fração de biomassa foi analisada por HPLC-DAD-ESI/MS, onde 17 compostos foram identificados na casca e 14 compostos na restante biomassa. Enquanto que na casca foram apenas idenditificados flavan-3-ols, na parte aérea a maior parte dos compostos são flavonoides (10 identificados), seguido de 2 flavan-3-ois e ainda 2 ácidos fenólicos, sendo o composto maioritário, nos dois casos, um dímero de procyanidina.

Para avaliar a biotividade dos extratos, realizou-se a análise antimicrobiana por microdiluição, utilizando bacterias Gram-positivas e Gram-negativas, isoladas de ambiente clínico e alimentar. A atividade antioxidante foi realizada por duas metodologías distintas: inibição da peroxidação lipídica em tecidos cerebrais de porco (TBARS) e inibição da hemólise oxidativa (OxHLIA), onde o extrato da casca de zimbro se mostrou mais promissor, apresentando um EC_{50} mais baixo (TBARS: $EC_{50}=11.30\pm0.88$ μg/mL e OxHLIA: 14.9 ± 0.5 μg/mL) em comparação com o extracto da parte aérea (TBARS: $EC_{50}=25.89\pm0.62$ μg/mL e OxHLIA: 47 ± 1 μg/mL). Por sua vez, a citotoxicidade foi avaliada numa cultura de células não tumorais: PLP2 (cultura primária de células de fígado de porco), em que ambos os extratos apresentaram toxicidade para esta linha celular. No entanto, de acordo com a aplicação-alvo, a toxicidade apresentada pelos extratos deve ser analisada mais profundamente, verificando esta condição em modelos de toxicidade específicos para cada indústria/produto. No geral, tendo em conta a composição química e as bioatividades comprovadas, os extratos quer da casca, quer da parte aérea do zimbro são potenciais matérias-primas para o desenvolvimento de produtos com aplicação na área alimentar, farmacêutica e/ou cosmética.

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Evaluación de la presencia de residuos de fungicidas e insecticidas en cerveza mediante cromatografía de líquidos y espectrometría de masas en tandem

Tania Arias, Leticia Pérez-Mayán*, María Ramil, Isaac Rodríguez

Department of Analytical Chemistry, Nutrition and Food Sciences, IAQBUS - Institute of Research on Chemical and Biological Analysis, Universidade de Santiago de Compostela, R/Constantino Candeira SN, 15782 Santiago de Compostela, Spain
**e-mail: leticia.perez.mayan@rai.usc.es*

Los pesticidas se usan extensivamente para proteger los cultivos en la agricultura. El uso de fitosanitarios está regulado a nivel europeo por el Reglamento (CE) nº 1107/2009 y el Reglamento (CE) nº 396/2005 [1,2]. La legislación vigente hace referencia a compuestos autorizados para su uso, dosis recomendadas, y valores máximos de residuos (MRLs) en productos de origen vegetal, entre ellos frutas, verduras y cereales [3]. Durante la producción de alimentos elaborados, una fracción de los pesticidas presentes en las materias primas usadas pueden pasar al producto final. En estos casos, la normativa no establece valores límites para los productos elaborados. Al objeto de fijar estos valores en un futuro, y evaluar el riesgo para los consumidores, se están tratando de establecer los denominados factores de transferencia, que hacen referencia a la relación de concentraciones existentes en el producto elaborado frente a las medidas en las materias primas de origen vegetal.

La cerveza es la bebida de fermentación más consumida a nivel mundial. Su proceso de elaboración es relativamente complejo, y multietapa, empleando dos grupos diferentes de materias primas de origen vegetal: el cereal (normalmente cebada) y las flores de lúpulo. Tanto el cultivo de cereales como del lúpulo emplea cantidades considerables de diversos pesticidas, y más concretamente de insecticidas y fungicidas. Una parte de estos compuestos podría alcanzar el producto final

El objetivo de este estudio es desarrollar un método multi-analito, que permita la determinación de residuos de pesticidas en muestras de cerveza con diferentes características en cuanto a su origen, contenido etanol, etc, con límites de cuantificación inferiores a 1 ng/mL. La selección de compuestos se ha realizado en función de los datos de consumo en el cultivo del cereal, disponibles en MAPA. El procedimiento diseñado contempla una etapa de concentración de las muestras mediante extracción en fase sólida, seguida del uso UPLC-QqQ-MS como técnica de determinación. En comparación con procedimientos previos, ej. método QuEChERS, se redujo el consumo de disolventes orgánicos y la manipulación de las muestras, manteniendo valores de exactitud en el rango de 80%-120% y alcanzando LOQs inferiores a 1 ng/mL, para la mayoría de los compuestos considerados. Una vez validado el protocolo analítico, se han procesado muestras de diferentes orígenes, identificando varios compuestos presentes de forma habitual en cervezas comerciales. Entre ellos destacan los fungicidas boscalid, dimethomorph, miclobutanil, boscalid y mandipropamida.

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Direct, automated and sensitive determination of glyphosate and related anionic pesticides in environmental water samples using SPE on-line combined with LC-MS/MS

Javier López-Vázquez, Leticia Pérez-Mayán*, Victoria Fernández-Fernández, Rafael Cela, Isaac Rodríguez

Department of Analytical Chemistry, Nutrition and Food Science. Research Institute for Chemical and Biological Analysis (IAQBUS), Universidade de Santiago de Compostela, Santiago 15782, SPAIN
**e-mail: leticia.perez.mayan@rai.usc.es*

Glyphosate (GLY) is worldwide employed as a non-selective weed killer in gardening and agriculture[1]. With the same aim, the limits of roads are often fumigated with this herbicide. The development of genetic modified (GMO) plants was a milestone in the use of GLY, allowing a significant reduction in the production costs of cotton, soya and maize, among others. As a result of these extensive uses, the risk of polluting surface water environments with this herbicide, and its degradation product aminomethylphosphonic acid (AMPA), is not negligible. Other species of environmental concern with similar chemical properties are the insecticide glufosinate and the fungicide degradation product Fosetyl-aluminum. This list is normally implemented with some additional transformation products, such as n-acetyl glufosinate (NAG) and 3-(methylphosphinic) propionic acid (MPPA).

Conventional strategies to the determination of glyphosate rely on compound derivatization followed by GC-MS(MS) or LC-MS(MS) determination, as function of the kind of derivatization strategy: formation of trifluorinated derivatives or fluorenemethoxy carbonyl species (FMOC), respectively. In both cases, derivatization is time-consuming and not always transposable to related pesticides and transformation products, as it is the case of their n-acetyl species or Fosetyl.

Thus, an automated procedure for the simultaneous determination of six anionic pesticides, including glyphosate (GLY) and AMPA, was developed and applied to the analysis of environmental water samples. The proposed method combines on-line concentration of water samples (0.160 mL), with compounds separation in an anion-exchange liquid chromatography (LC) column, followed by their selective determination by tandem mass spectrometry (MS/MS). The global procedure was completed in 25 min, providing limits of quantification (LOQs) between 5 ng L^{-1} and 20 ng L^{-1}, with reduced effect of the surface water matrix in the efficiency of process (SPE and ionization yields).

The method was applied to the analysis of grab samples obtained from three watersheds, in two rural and one residential area, in Galicia (North-west Spain). Out of six investigated compounds, Fosetyl, AMPA and GLY were noticed in the set of processed samples. Their detection frequencies increased from 12% (Fosetyl) to 88% (AMPA). Median concentrations followed the same trend varying from 9 ng L^{-1} (Fosetyl) to 44 ng L^{-1} (AMPA). The higher levels and the large seasonal variations in the residues of the latter species were noticed in small rivers affected by discharges of municipal sewage treatment plants (STPs).

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Comprehensive characterization of volatile and semi-volatile compounds in e-liquids formulations for electronic cigarrettes by gas chromatography accurate mass spectrometry

M. Cobo-Golpe, A. González-Rodríguez, M. Ramil, R. Cela, I. Rodríguez

[1]Department of Analytical Chemistry, Nutrition and Food Science. Research Institute for Chemical and Biological Analysis (IAQBUS), University of Santiago de Compostela, Santiago 15782, SPAIN
**e-mail: miguel.cobo.golpe@usc.es*

Electronic cigarrettes (e-cigarrettes) have been developed as a healthier alternative to tobacco, aiming to reduce human exposure to harmful compounds present in conventional cigarrettes, including nicotine. The e-cigarrette device includes a battery and a resistance to heat a reservoir containing a solution of different compounds dissolved in a mixture of glycerin and propylene glycol. Air is inhaled through the heated e-liquid generating a vapor containing different flavors. Currently, a broad range of e-liquids compositions are available in the market, with or without nicotine, and with the possiblity of also introducing non-psycotropic derivatives of cannabis, such as cannabidiol (CBD). As a general statement, all the ingredients included in e-liquid formulations are recognized as safe, since they are authorized to be used as flavors and/or additives in food products; nevertheless, some of them might lead to respiratory problems when inhaled. Furthermore, the complete characterization of minor compounds existing in these mixtures, and the identification of potential reaction derivatives is a complex task, which requires further research and data.
In this study, we evaluate the possibilities of gas chromatography combined with a time-of-flight mass spectrometry system (GC-TOF-MS) for the comprehensive characterization of e-liquid formulations. Commercial samples were diluted with ethyl acetate and processed by GC-TOF-MS, using two different capillary columns with complementary selectivity. Thereafter, raw MS spectral data was de-convoluted and the obtained spectra were compared to those existing in commercial low resolution and an in-house accurate databases. Reliability of tentative identifications was improved with retention index values. Combining the information provided by both capillary columns (Carbowax and HP-5 types), for a selection of 40 e-liquids, around 300 compounds were tentatively identified (150 compounds using HP-5, 60 compounds using Carbowax and 75 compounds with both columns). Their accurate spectra and retention index were gathered in two databases, which might be useful for other researchers. Some minor compounds, i.e. certain alkaloids, were identified as associated to nicotine containing e-liquids. In the same way, several compounds structurally related to cannabidiol (i.e. the cyclization derivative cannabielsoin and others with a shorter alkylated chain) can be considered as markers of the use of cannabis extracts in e-liquids. Finally, some of the compounds identified in GC-TOF-MS chromatograms are potential artefacts (such as acetals of major aldehydes existing in e-liquids or tetrahydrocannabinol), generated in the hot injector of the GC-MS instrument. Further research is required to assess whether such reactions might also take place during volatilization of e-liquids in the e-cigarette device.

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Estudio espectrofluorimétrico del pesticida imidacloprid y su principal metabolito el ácido 6-cloronicotínico

Rodríguez-Cáceres, M.I.*, Mora-Díez, N.M., Simón-García, D.

[1]Departamento de Química Analítica e Instituto de Investigación del Agua,
Cambio Climático y Sostenibilidad (IACYS)
Av. Elvas, s/n, 06006 Badajoz, España
*maribelro@unex.es

El imidacloprid (IMI) es el representante principal de la familia de los pesticidas neonicotinoides, los cuales están estructuralmente relacionados con la nicotina. IMI tiene un metabolito principal, que es el ácido 6-cloronicotínico (6-ACN).

Estos pesticidas tienen grandes ventajas en cuanto a su selectividad, alta solubilidad en agua, modo de empleo y baja toxicidad para mamíferos, aves y peces. Por eso el imidacloprid se ha convertido en el segundo pesticida más vendido en el mundo. Sin embargo, su uso excesivo está causando problemas tanto en algunos animales como en los consumidores. Por lo tanto, dadas estas preocupaciones, es importante continuar investigando el impacto ambiental de estos pesticidas, y es necesario proponer métodos para determinarlos que ayuden a controlar sus residuos en muestras ambientales [1].

El objetivo de este trabajo fue desarrollar nuevos métodos analíticos para la determinación de IMI y 6-ACN en muestras de agua potable. Ambos compuestos fueron estudiados por fluorescencia molecular y fluorescencia fotoinducida. Una vez optimizados los parámetros químicos e instrumentales, se construyeron las curvas de calibración utilizando el método de patrones externos para ambos analitos. Asimismo, se realizó el correspondiente estudio de linealidad y repetibilidad. Para IMI se obtuvo un rango lineal entre 50,0 y 200,0 ppb, con LOD de 15,8 ppb calculado con el método de Clayton. Para el 6-ACN, el rango lineal estuvo entre 1,0 y 5,0 ppm, con LOD superiores a los del IMI, en concreto 171,3 ppb calculado por el mismo método. Finalmente, se realizó un estudio de interferencia de cada analito.

Una vez realizados todos los estudios previos y comprobado que no existían interferencias en la determinación de ambos analitos, se propusieron dos métodos, uno para la determinación de IMI mediante fluorescencia fotoinducida y otro para la determinación de 6-ACN mediante fluorescencia molecular. Los dos métodos desarrollados se aplicaron para la determinación de IMI y 6-ACN en muestras de agua potable, obteniendo una recuperación media de IMI entre 108 y 122% y entre 67 y 99% para 6-ACN. Estas recuperaciones están de acuerdo con las encontradas en la bibliografía [2,3].

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Time-Resolved Fluorescence Excitation-Emission spectroscopy and PARAFAC to solve overlapping signals

L.A. Sarabia[1,*], L. Rubio[2], S. Sanllorente[2], M.M. Arce[2], M.C. Ortiz[2]

[1]Universidad de Burgos, Dpto. Matemáticas y Computación, Plaza Misael Bañuelos, s/n 09001 Burgos, España
[2]Universidad de Burgos, Dpto. Química, Plaza Misael Bañuelos, s/n 09001 Burgos, España
**e-mail: lsarabia@ubu.es*

This work shows the possibility to resolve the composition of mixtures, which contain analytes with identical excitation-emission spectra, using Time-Resolved Fluorescence Excitation-Emission (TREEM) [1,2] together with PARAFAC decomposition. Measured decay time-resolved fluorescence spectroscopy works based on the duration of the excitation state where the variation is of only a few nanoseconds so measurable changes can provide additional structural information about the analytes. The compounds analyzed belong to quinolones group (enrofloxacin and ciprofloxacin) widely used in poultry farms which presence must disappear after their use to ensure public health.

Mixtures of both analytes were prepared in acetic acid-acetate buffer solution pH 4 and were analyzed using a modular fluorescence spectrometer (Edinburgh Instrument FLS980) equipped with a 280 nm laser as the excitation light source. The dimension of the three-way array used was (42×2048×16), where the first dimension corresponded to the emission profile (recorded between 350 and 550 nm), the second one corresponded to the lifetime (between 0 and 20 ns) and the third one was the sample profile (the mixtures prepared in the laboratory).

The CORCONDIA index of the two-factor PARAFAC model obtained from the decomposition of that three-way array was 99%. The quantification of both analytes has been possible despite their lifetimes are so similar as can be seen in Fig. 1A (1.378 and 2.160 ns). The factors in blue and red in the sample profile (Fig. 1B) correspond to enrofloxacin and ciprofloxacin, respectively.

This research opens an interesting way to analyze fluorescent analytes that share identical excitation-emission spectra and could not be identified with the molecular fluorescence technique even using PARAFAC. The use of the lifetime, as a third PARAFAC profile, has solved this problem.

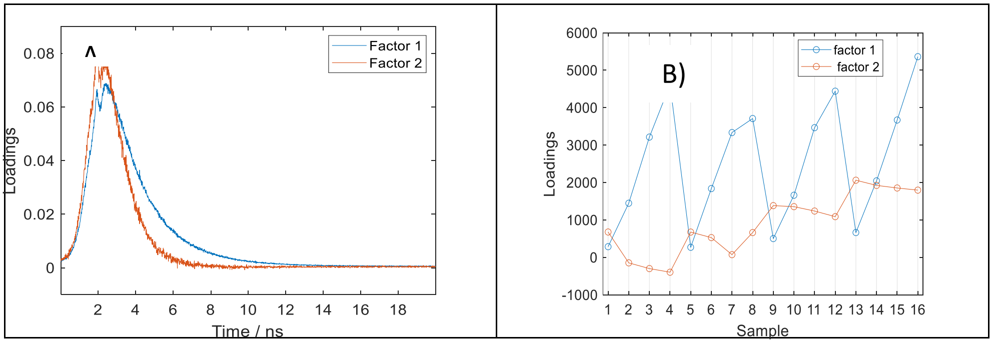

Fig.1. Loadings of the PARAFAC model: factor 1 (enrofloxacin), factor 2 (ciprofloxacin). Loadings of the fluorescence decay lifetime profile (A); sample profile (B).

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Analytical Quality by Design for selecting optimal experimental conditions of a head space-solid phase microextraction for several phthalates analyzed by CG-MS

L. Valverde-Som[1], A. Herrero[1], C. Reguera[1], L. A. Sarabia[2], M. C. Ortiz[1], M. S. Sánchez[2]

[1]Universidad de Burgos, Dpto. Química, Plaza Misael Bañuelos s/n, 09001 Burgos, España
[2]Universidad de Burgos, Dpto. Matemáticas y C., Plaza Misael Bañuelos s/n, 09001 Burgos, España
**e-mail: lvalverde@ubu.es*

Analytical Quality by Design (AQbD) is the version of QbD applied to the development of an analytical method or procedure. The main idea is to develop the analytical method in such a way that the desired quality, expressed in terms of the so-called Analytical Target Profile (ATP), is maintained while allowing some variations in the Control Method Parameters (CMP). The present work presents a general method for obtaining the CMP corresponding to a preset ATP by inverting a PLS2 model [1-2].

In particular, the methodology is applied for selecting optimal experimental conditions in a head space-solid phase microextraction (HS-SPME) procedure for the simultaneous determination by GC-MS of 4 phthalates used as plasticizers (diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis(2-ethylhexyl) phthalate (DEHP)), and the corresponding internal standard (diisobutyl phthalate-3,4,5,6-d_4 (IS)). Almost all these phthalates are toxic (category 1B) with endocrine disrupting properties according to Regulation (EC) No 1907/2006 [3].

In short, a multivariate-multi-response predictive model must be fitted to estimate the expected quality as a function of the process variables, temperature and time of extraction (the CMP), used in the HS-SPME step. The main goal is to maintain a given quality, as stated in the multivariate ATP, which cannot be directly modified but indirectly via the CMP. Therefore, the inversion of the prediction model is needed to determine the values of the CMP for which the given ATP is fulfilled.

Consequently, the proposed procedure has two steps: i) with the CMP (in this case, temperature and time, set at 3 and 6 levels, respectively) to experimentally obtain **Y** (related to the recovery for the five simultaneously analyzed compounds), and then fit a PLS2 model to predict the analytical responses in **Y**, and ii) to invert the PLS2 prediction model, looking for the Pareto front of the five responses. The Pareto front contains the set of experimental conditions (temperature and time of extraction) to conduct the HS-SPME so as to simultaneously maximize the recovery of the five compounds being measured.

The global PLS2 model fitted to simultaneously predict responses for the 5 compounds, has 3 latent variables, and determination coefficient R^2 (in training) equal to 0.93 (0.97, 0.95, 0.96, 0.89, and 0.92 for each individual response related to DEP, IS, DBP, BBP, and DEHP, respectively). During the experimentation, the last two compounds prove to be those with the lowest sensitivity, so the PLS2 model is inverted to obtain at least 50 % of each individual maximum value in **Y**. The resulting optimal experimental conditions give expected responses fulfilling the ATP with around 45 minutes at 79 ºC, so reducing almost to the half the time of analysis.

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Deseño de fase estacionaria para a separación de nanopartículas metálicas mediante cromatografía líquida

Iván Lozano González[1,*], **Alvaro Gil**[2], **Francisco Guitián**[2], **Pilar Bermejo Barrera**[1], **Antonio Moreda Piñeiro**[1]

[1]Grupo de Elementos Traza, Espectroscopía e Especiación (GETEE), Instituto de Materiais iMATUS, Departamento de Química Analítica, Nutrición e Bromatoloxía, Facultade de Química, Universidade de Santiago de Compostela, Avenida das Ciencias, s/n 15782 Santiago de Compostela, España
[2]Instituto de Cerámica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, España
**ivan.lozano.gonzalez@rai.usc.es*

Durante as últimas décadas, a industria das nanopartículas non fixo mais que crecer ano tras ano, e con este aumento da produción, debemos destacar a necesidade de investigar se estas poden chegar a producir algún tipo de adversidade tanto para o medio ambiente coma, finalmente, á propia saúde humana.

Se ben é certo, as múltiples aplicacións que se lles da a día de hoxe en campos tales coma a medicina (distribución de medicamentos de maneira localizada, terapia antitumoral, terapia antibiótica), aplicación en fabricación e materiais (informática, produtos de acotío, sensores químicos e biosensores), aplicación medioambiental (interacción de contaminantes coas nanopartículas para facilitar súa eliminación do medio), electrónica, xeración de enerxía (xeración mediante fotoelectroquímica e división electroquímica do auga), industrias mecánicas (nanopartículas actuando coma recubrimento, lubricante e adhesivos). [1]

Por iso mesmo é importante levar a cabo unha correcta detección e determinación destas nanopartículas que podan estar presentes nos medios naturais. Para elo, vaise empregar un sistema híbrido de HPLC-ICP-MS. A columna empregada ten unha fase estacionaria a base de esferas de vidro inertes. A mostra que se fai pasar pola columna trátase dunha disolución de nanoparticulas de prata de 40 nm a diferentes concentracións dopada con prata iónica.

Tras varias medidas chegouse a lograr separar as nanopartículas da mostra iónica empregando auga mili-q como fase móbil e con un fluxo elevado (0,9-1 mL min^{-1}). No cromatograma soamente se obtiña un pico cromatográfico ao inxectar soamente as nanopartículas e, por outra banda, cando se inxecta a prata iónica non se logra rexistrar ningún pico en absoluto. Cando inxectamos unha mestura das dúas mostras o resultado volve a ser un único pico que coincide en tempo de retención (t_R) a cando se inxectaron soamente as nanopartículas. Tras estes resultados puidemos determinar que con este método é posible chegar a separar as nanopartículas da forma iónica do propio metal.

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Evaluation of agriculture plastics as vehicles of pesticides and concerning pollutants in the environment

M. Cobo-Golpe, M. Ramil, R. Cela, I. Rodríguez

Department of Analytical Chemistry, Nutrition and Food Sciences. Research Institute on Chemical and Biological Analysis (IAQBUS). Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain.

(Email: miguel.cobo.golpe@usc.es)

Modern agriculture employs large amounts of polymeric materials to enhance the productivity of crops and to facilitate their management. Among others, it is particularly important the use of mulching films, to prevent the development of grass in horticulture crops; anti-frost nets, water and nutrient distribution pipes, tree protection tubes and agriculture tape tie. During their useful life, these polymeric items are in direct contact with the range of pesticides applied to crops. Obviously, these compounds might remain adsorbed in plastic goods and might be transferred to soil, or even to surface water, due to soil erosion during intense run off events. As a general statement, the smaller the size of the employed plastic items, the more difficult it is to recover these materials from fields, and thus, the higher the risk to be fragmented to micro- and nano-plastics during their aging under environmental conditions.

In addition to adsorbed compounds, plastics employed in agriculture include a number of additives to enhance their useful life and to improve their stability. Among others, the use of antioxidants, i.e. phosphite-type species and UV filters is well-documented. In this case, either the parent compounds or their transformation products (tri-substituted phosphates arising from oxidation of phosphites) might migrate from the host material to agriculture soil. The larger the area of contact between both media, the higher the migration risk. Thus, soil covering films and silage wrapping plastics represent concerning cases. In addition to compounds intentionally added to agriculture polymers during their production, the increasing importance of the plastic recycling industry might result in the presence of unwanted compounds in new plastic materials.

The aim of this presentation is to provide an overview of the presence of a selection of pesticides and polymer additives in different types of plastic items designed for agriculture uses. Both, virgin plastics and polymeric materials obtained from agriculture fields were extracted and processed using orthogonal analytical techniques. Particularly, potential pesticide residues will be investigated using a target MS/MS method following a LC separation step. Furthermore, a non-target screening workflow using gas chromatography (GC) combined with accurate MS detection was used to identify semi-volatile additives in new and used agriculture plastics. The range of pesticides found in items collected from fields includes several fungicides, with Folpet showing the highest residues. In contact with model water solutions, up to 40% of several pesticides migrated from polypropylene items (tree protection tubes) to the water phase. Traces of certain pesticides were also found in new materials, such as irrigation pipes, mulch film and tie tape. Regarding polymer additives, benzotriazole-type UV filters and tris-(2,4-ditert-butylphenyl) phosphate were those showing the highest concentration levels (in some cases above 100 mg/Kg) in virgin and used agriculture plastics.

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SINGLE-CELL-ICP-MS MEASUREMENTS FOR STUDYING SILVER NANOPARTICLES INTERNALIZATION IN CELL LINES FROM SEA-BASS AND CLAMS

C. Suárez-Oubiña*[1], A. Moreda-Piñeiro[1], P. Herbello-Hermelo[1], P. Bermejo-Barrera[1], N. Mallorca[2], M. Vázquez[2], S. Cabaleiro[2]

[1] Trace Element, Spectroscopy and Speciation Group (GETEE), Institute of Materials (iMATUS), Department of Analytical Chemistry, Nutrition and Bromatology. Faculty of Chemistry. Universidade de Santiago de Compostela. Avenida das Ciencias, s/n. 15782, Santiago de Compostela. Spain

[2] Ctr Tecnol Cluster Acuicultura, Cluster Acuicultura, Punta Couso S-N, Ribeira 15965, Spain

**cristiansuarez.oubina@usc.es*

Introduction

Metal and metal oxide nanoparticles (NPs) have been widely used due to their exceptional physicochemical properties. Large-scale production and use will result in the release of these particles into the environment. Therefore, data are necessary for evaluating the environmental risk of these emerging pollutants, especially regarding the uptake and biological effects. *In vitro* assays can provide significant information on how these NPs are capable to be internalised in cells as a previous stage for elucidating the bioaccumulation in fish and molluscs and also the bioavailability in humans.

Single-cell-inductively coupled plasma – mass spectrometry (SC-ICP-MS) has opened a new area of research which allows the quantification of metals in single biological cells at ultra-low levels, sensitive determination not provided by other instrumental techniques. Therefore, the aim of the current research has been to explore the possibilities of SC-ICP-MS to assess Ag NPs inside kidney cells from sea-bass (*Dicentrarchus labrax*) and clams (*Ruditapes philippinarum*) as a previous stage for performing bioaccumulation studies of Ag NPs in these cultured species.

Methods and results

Kidney sea-bass and clam cells were exposed to Ag NPs (15 and 100 nm) at different NPs concentrations and exposure times, and the internalization of Ag NPs in each single cell was assessed by SC-ICP-MS.

Several parameters regarding SC-ICP-MS were studied with the aim of developing a novel, high sensitivity and accurate method for assessing Ag NPs in single cells from aquaculture products. Properly cell concentration and dwell time were optimised for avoiding multi-cell coincidence. In addition, the effect of washing stages (1% PBS) was tested in order to remove non-internalised Ag NPs and/or Ag NPs adsorbed onto the cell's surface. This procedure helps to avoid high dissolved backgrounds, possible interferences, or excess particles that could mask the signal generated by the single cells.

Optimised SC-ICP-MS conditions were applied for assessing the rate of internalization of Ag NPs of different size distributions based on the concentration and exposure time.

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Statistical experimental design to determine phenolic compounds in seawater by the AgNPs synthesis

M.C. Prieto-Blanco*, I. Correa-Comesaña, A. Carlosena-Zubieta, S. Muniategui-Lorenzo

[1]University of A Coruña, Grupo Química Analítica Aplicada (QANAP), University Institute of Research in Environmental Studies (IUMA), Department of Chemistry. Faculty of Sciences, Campus de A Coruña, s/n, 15071, A Coruña, Spain.
**m.c.prieto.blanco@udc.es*

Currently, there is a general trend to develop *in-situ* analysis methods which provide rapid information on the environmental pollution. In this regard, the use of nanomaterials for the sensor design or the nanoparticles formation in solution are some of the possible strategies.

In order to establish a simple, fast and economic analytical methodology for the determination of phenolic compounds in environmental samples, a design of experiments (DoE) was used to find out the variables with statistically significance effects on AgNPs synthesis by the reduction of silver nitrate using pyrogallol as reducing agent in alkaline medium [1]. This study was carried out, simultaneously, using ultrapure water and seawater. The pyrogallol could be quantified by the surface plasmon resonance (SPR) measurement of the AgNPs using UV spectrophotometry (UV-vis).

A 2^3 Plackett-Burman design [2] was applied considering as variables: the concentrations of $AgNO_3$, pyrogallol and NaOH, and the order of addition of sodium hydroxide. The results show that the concentrations of pyrogallol and silver nitrate have a significant effect ($P<0.05$), although slight differences were observed between synthesis in ultrapure water and seawater. The highest assayed concentrations of silver nitrate (700 µM) and pyrogallol (700 µM) favoured the formation of AgNPs in both matrices. Regarding NaOH concentration (6-36 mM), it had a positive effect in seawater and a negative effect in ultrapure water. The order of addition was no significant, although it was dependent on the reagent concentration range. Interactions between the variables have also been studied.

In this way, the appropriate conditions for the determination of a phenolic compound, pyrogallol, in a complex environmental matrix, seawater, were established and samples from the vicinity of A Coruña port areas were analyzed. The standard addition method was required~~.~~ The estimated limits of detection were around 25 µM (3 mg/L).

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MATRIX SOLID-PHASE DISPERSION AND ULTRASOUND-ASSISTED EXTRACTION IN THE EXTRACTION AND POLYPHENOLIC CHARACTERISATION FROM FIVE VARIETIES OF BROWN ALGAE

Aly Castillo[1,2], Kristina Grgić[3], María Celeiro[1,2], Carmen Garcia-Jares[1,2], Stela Jokić[3], Marta Lores[2]

[1]CRETUS, Departamento de Química Analítica, Nutrición y Bromatología, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España.
[2]LIDSA, Departamento de Química Analítica, Nutrición y Bromatología, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España
[3]Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhaca 20, 31000, Osijek, Croatia
alyjesus.castillo.zamora@usc.es

Among the broad group of phytochemical compounds, polyphenolic structures are of special interest due to their bioactive capacity, being important antioxidants associated with beneficial effects on health [1]. Although the potential of brown algae to contain these compounds is well known, research on their polyphenolic potential is still scarce [2]. At the same time, phenolic chains present a structural variety that confers them a heterogeneous affinic profile towards the different solvents used for their extraction, playing a key role both in the recovery and in the bioactive properties of the extracts obtained [3]. In this work, the total polyphenolic content of five brown algae: *Dictyota dichotoma, Cystoseira barbata, Cystoseira spicata, Ellisolandia elongata* and *Sargassum sp.* is evaluated and characterised, as well as the effect of the extractive solvent on their recovery. In this way, the solvents methanol, ethanol, and water, were selected as extractants in the application of the techniques Matrix Solid-Phase Dispersion (MSPD) and ultrasound-assisted extraction (UAE) (Fig.1), using as indicators of the extractive efficiency the bioactive properties total polyphenolic content (TPC) and antioxidant activity (AA), and the individual polyphenolic profile analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The results showed a wide range of TPC from 0.20 mgGAE·g^{-1} for the methanolic extract of *E. enlongata* to 38 mgGAE·g^{-1} corresponding to the aqueous ethanolic extract of *Sargassum sp.* In general, the isovolumetric ethanolic ratio shows a better overall recovery of phenolic compounds, the macroalga *D. dichotoma* being the exception, improving its TPC by 20% when methanol is applied as extractant. At the same time, a higher extractive and bioactive efficiency of the extracts is obtained using UAE compared to MSPD. According to their individual profiles, hydroxybenzoic acid and some of its derivatives, as well as other bioactive compounds of interest, have been detected in all the species studied, providing a better knowledge of the bioactive content of these macroalgae species, and their potential application to the nutraceutical sector.

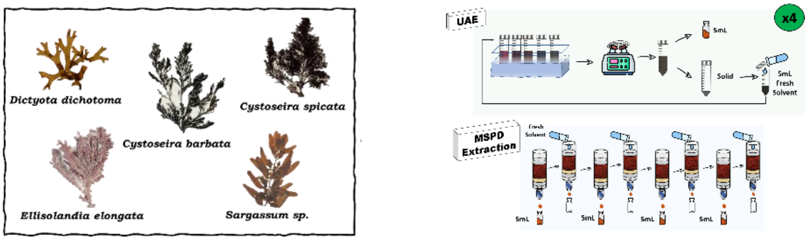

Fig.1. Comparative analysis of matrix solid-phase dispersion and ultrasound-assisted extraction techniques in the sequential extraction of 5 varieties of brown algae.

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Determinación de nanopartículas de dióxido de titanio en piensos empleados en acuicultura

A. Justo-Vega*, D. Padín-Villa, M.R. Domínguez-González, A. Moreda-Piñeiro, P. Bermejo-Barrera

Facultad de Química, iMATUS, Avda. de las Ciencias s/n, Santiago de Compostela, España
**ana.justo.vega@rai.usc.es*

La acuicultura juega un papel muy importante en la producción de alimentos de elevado nivel nutricional en línea con los objetivos de desarrollo sostenible de la agenda 2030 de las Naciones Unidas (ONU) [i]. Por otro lado, es de destacar la gran importancia económica de esta industria en España donde se cosecha un 23% del total de la UE, y de forma particular en Galicia que exporta más del 65% de su producción de rodaballo a mercados internacionales (99% de la producción española) [ii]. Este sector se enfrenta a importantes retos científicos y tecnológicos que debe superar para poder seguir creciendo de forma sostenible y rentable. La nanotecnología tiene aquí un importante papel, tanto en la producción como en la conservación, transporte y trazabilidad de sus productos. De forma particular, las nanopartículas de dióxido de titanio (TiO_2 NPs), gracias a sus propiedades fotocatalíticas, se emplean para garantizar la calidad microbiológica del agua de cultivo y en envases para su comercialización. Del mismo modo, las TiO_2 NPs, se emplean en piensos para evitar el crecimiento de bacterias y hongos mientras están almacenados, y se está estudiando su uso en piensos para tratar enfermedades bacterianas de los peces. Sin embargo, a pesar de que el TiO_2 en su forma masiva no es tóxico, está siendo evaluado en su forma nanoparticulada. Existen estudios que muestran que los peces pueden acumular Ti a partir de su exposición a TiO_2 NPs a través del pienso [iii] y, dado que el riesgo toxicológico de las NPs [iv] depende también del tamaño de éstas, es necesario el desarrollo de metodologías analíticas que permitan determinar tanto el contenido de las TiO_2 NPs como su tamaño en el alimento suministrado.

En este trabajo se presenta la optimización de un método de extracción de TiO_2 NPs de piensos empleados en acuicultura mediante lixiviación alcalina (hidróxido de tetrametilamonio, TMAH) como extractante asistida por ultrasonidos para reducir el tiempo de extracción y aumentar la eficacia del proceso. La determinación de la concentración de TiO_2 NPs y del tamaño de éstas en el extracto se ha realizado por espectrometría de masas con plasma de acoplamiento inductivo operando en detección de partículas individualizadas (spICP-MS).

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Revisión bibliográfica del empleo de reacciones fotoquímicas en electroanálisis

Mora-Diez, N.[*], **Rodríguez-Cáceres, M.I., Llanos-Toro, M.**

Departamento de Química Analítica e Instituto de Investigación del Agua,
Cambio Climático y Sostenibilidad (IACYS)
Av. Elvas s/n, 06006 Badajoz, España.
**nielene@unex.es*

Las reacciones fotoquímicas han sido utilizadas con diversos objetivos, ya sea para el pretratamiento de las muestras, con la consiguiente eliminación de componentes indeseables de la matriz donde se encuentran los analitos; o para acelerar una reacción y así acortar el tiempo de análisis; o para producir analitos medibles o más fácilmente medibles por el detector seleccionado.

En general, se plantean varios tipos posibles de esquemas para las reacciones fotoquímicas, cuando se utilizan con el objetivo de obtener un producto cuya señal analítica sea medible con el detector seleccionado [1].

Los tipos principales de reacciones que se emplean en procesos fotoquímicos son: reacciones de fotociclación, fotoisomerización, fotólisis, fotooxidación y fotoreducción.

Las reacciones fotoquímicas han sido detectadas midiendo señales de diverso tipo, como señales fotométricas [2], de fluorescencia [3], electroquímicas.

Dentro del análisis fotoquímico, la Foto-Voltamperometría ha recibido una menor atención en comparación con otros métodos. Ha sido utilizada con distintos fines como:

a) Eliminación de materia orgánica para la determinación de iones metálicos
b) Determinación de sustancia electroinactivas
c) Determinación de compuestos orgánicos inestables
d) Determinación indirecta de otras especies

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Electrochemical evaluation of the psychoactive recreational drug 4-bromo-2,5-dimethoxyphenethylamine (2C-B)

Daniel Martins[1], E. Manuela Garrido[2], Fernanda Borges[1], Jorge Garrido[2,*]

[1]CIQUP-IMS, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
[2]CIQUP-IMS, Department of Chemical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Rua Dr. Bernardino de Almeida 431, 4249-015 Porto, Portugal
**jjg@isep.ipp.pt*

New psychoactive substances (NPS) are a growing concern worldwide today. By December 31st 2021, over 884 NPS were being monitored by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) [1]. The number of NPS notified in 2021 continues the trend seen since 2016 of around 50 new substances appearing for the first time each year [1].

Amphetamine and phenethylamine derivatives are synthetic drugs with high prevalence of abuse worldwide, particularly among young adults. Recreational use of this family of substances had revolved around a few compounds, mainly 3,4-methylenedioxymethamphetamine (MDMA, ecstasy), methamphetamine (ice, crystal) and amphetamine, although at least 200 different synthetic phenethylamines and tryptamines have been synthesized and their psychoactivity described. 4-Bromo-2,5-dimethoxyphenethylamine (2C-B, Nexus, Afro) is one of these synthetic drugs. 2C-B gained certain popularity as a legal substitute for MDMA after its prohibition in 1985 [2]. 2C-B was legal in most countries until the mid-1990s, when it became a controlled drug in most countries. 2C-B has been intermittently detected in the illegal drug market in several countries over the last decades

Regarding current prevalence and pattern of use, very little information is available dealing specifically with 2C-B, despite the efforts of several organizations such as the EMCDDA.

Electrochemical methods have become popular because they are inexpensive, easy to handle, and fast and allow obtaining relevant data for the study of drugs' metabolism. Electrochemistry allows predicting and anticipating the process of biotransformation that a molecule can suffer in the human body as well as the common transformation products that can coexist with the drug.

The goals of the present work were to explore the electrochemical profile of 2C-B in order to contribute to a more detailed understanding of phenethylamine derivatives' biotransformation and to the development of new electrochemical sensors with improved sensitivity. The results obtained will be presented in this communication.

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Microencapsulation of benzyl isothiocyanate using β-cyclodextrins

Taynara Araújo[1], E. Manuela Garrido[1,*], Alexandra Gaspar[2], Fernanda Borges[2], Jorge Garrido[1]

[1]CIQUP-IMS, Department of Chemical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Rua Dr. Bernardino de Almeida 431, 4249-015 Porto, Portugal
[2]CIQUP-IMS, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal
**emg@isep.ipp.pt*

A wide variety of plant-based compounds, known as phytochemicals, have been identified as being beneficial to human health. Naturally produced by plants, glucosinolates are sulphur-containing secondary metabolites, which are widely found in the Cruciferae (Brassicaceae) family of plants. Glucosinolates are physiologically inactive chemicals, but once they are hydrolyzed by myrosinase enzyme, they are converted into biologically active compounds such as isothiocyanates (ITCs). Isothiocyanates have been referenced to exhibit anti-inflammatory, antimicrobial, neuroprotective, and cardioprotective properties [1]. Despite having excellent biological features, ITCs have strong volatility and por bioavailability which hinders their potential use as effective bioactive agents.

Cyclodextrins are valuable natural or synthetically modified cyclic oligosaccharides that are widely used for ameliorating properties of biologically active compounds. They protect these compounds against light and oxidative degradation and provide host–guest supramolecular complexes having controlled release properties by molecular encapsulation, enhancing the water solubility and bioavailability [2].

In the present work, different techniques have been used and compared to optimize the microencapsulation conditions for the formation of benzyl isothiocyanate (BITC) inclusion complexes using different β-cyclodextrins. The results found showed that the use of ultrasonication had no significant effect on the dissolution of BITC, in addition to increasing the reaction rate. The results obtained will be presented in this communication.

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Determinación de medicamentos en aguas superficiales mediante inyección directa en cromatografía de líquidos acoplada a espectrometría de masas

J. Lejo-Santiago[1,*], E. Concha-Graña[1], P. López-Mahía[1], S. Muniategui-Lorenzo[1]

[1]Universidad de la Coruña, Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medioambiente (IUMA), Departamento de Química, Facultad de ciencias, Campus de A Coruña, s/n, 15071, A Coruña, España
**jorge.lsantiago@udc.es*

El desarrollo industrial y el aumento poblacional ha conllevado la aparición de un gran número de nuevas sustancias, muchas contaminantes, por lo que es importante el desarrollo de técnicas analíticas eficaces para su detección. Estas sustancias son conocidas como contaminantes de interés emergente (CEC), entre ellos se encuentran los medicamentos y sus metabolitos [1].

Estos medicamentos llegan al medio por dos vías principalmente, la primera es por residuos generados en hospitales, laboratorios y actividad ganadera y la segunda por excreción de los mismos tras su uso, a través de aguas residuales. Algunos compuestos que no son eliminados durante el tratamiento en las plantas depuradoras pueden finalmente contaminar las aguas superficiales [2]. En este trabajo se pone a punto un método multirresiduo, rápido y sensible mediante cromatografía de líquidos de alta eficacia acoplada a espectrometría de masas de triple cuadrupolo LC-MS/MS (QqQ) para la determinación de fármacos en aguas superficiales. Se analizaron 59 medicamentos que incluyen antibióticos, psicolépticos, analgésicos, antiinflamatorios, medicamentos para el sistema cardiovascular y antitrombóticos entre otros. El método propuesto emplea la inyección directa de 100 µl de muestra como alternativa a la etapa de pre-concentración, permitiendo alcanzar límites de cuantificación en el rango de <5 ng/L para la mayoría de analitos, por lo que se considera adecuado para la monitorización de estos compuestos en muestras ambientales.

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Firefighters’ personal exposure to airborne polycyclic aromatic hydrocarbons during controlled forest fires

Gabriel Sousa, Joana Teixeira, Cristina Delerue-Matos, Simone Morais, Marta Oliveira*

REQUIMTE/LAQV, Instituto Superior de Engenharia, Instituto Politécnico do Porto, Porto, Portugal
** E-mail: marta.oliveira@graq.isep.ipp.pt*

Portugal is among the southern European countries severely affected by wildfires [1]. During fire combat, firefighters are exposed to several hazards including particulate matter, heavy metals, and many volatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs) [2-3]. PAHs are persistent organic pollutants formed during the combustion of organic matter and are known for being endocrine disruptors with toxic, mutagenic, and carcinogenic properties [3,4]. Information related to Portuguese firefighters’ occupational exposure to PAHs during firefighting is inexistent. Thus, this work aims to determine the levels of 18 PAHs, 16 priority pollutants, benzo(j)fluoranthene, and dibenzo(a,l)pyrene, in the personal air of firefighters during controlled fires.

A total of 5 firefighters agreed to use a pre-cleaned polyurethane foam plug (PUF) attached to the personal protective equipment (PPE) at the breathing air zone during a controlled fire that occurred in Marco de Canaveses (North of Portugal) in January 2022. The passive air sampling campaign was performed during the entire fire event. Microwave-assisted extraction was used to extract the 18 PAHs from the sampled PUFs and extracts were analyzed in a C18 column with a liquid chromatography system equipped with a photodiode array and fluorescence detectors on line, according to previous work of the research team [5].

Among the 18 compounds under study, naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, and benzo(a)pyrene were detected in the personal air of all firefighters; acenaphthene, chrysene, and dibenzo(a,h)anthracene were not detected. Benzo(a)pyrene, the PAH classified as a carcinogen to humans (Group 1; [6]) was detected in 100% of the samples with values varying between 0.042 to 0.262 $\mu g/m^3$. Benz(a)anthracene, benzo(b+j)fluoranthene, benzo(k)fluoranthene, dibenzo(a,l)pyrene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene, possible or probable carcinogenic PAHs were also detected in the personal air of firefighters during firefighting. Recently the International Agency for Research on Cancer classified occupational exposure as a firefighter as carcinogenic to humans (Group 1) due to sufficient evidence for the development of mesothelioma and bladder cancer [2]. This preliminary study demonstrates firefighters´ exposure to PAHs during fire events, however additional studies are needed to better characterize exposures and estimate the associated potential health risks.

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O uso de uma sonda raciométrica combinando pontos quânticos de carbono e de $AgInS_2$ para a determinação de histamina recorrendo a modelos quimiométricos

<u>David S.M. Ribeiro</u>[1*], Rafael C. Castro[1], Ricardo N.M.J. Páscoa[1], João L.M. Santos[1]

[1] LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal
**dsmribeiro@gmail.com*

A histamina é uma amina biogénica que tem um papel fundamental em processos bioquímicos de resposta imunológica sendo também relevante em outras funções tais como, contração muscular, aumento da permeabilidade vascular e secreção do ácido gástrico, podendo atuar como neurotransmissor [1]. A histamina pode surgir em alguns alimentos tais como, frutas e peixes devido à descarboxilação da histidina livre através do metabolismo bacteriano. O consumo de alimentos ricos em histamina pode ter efeitos adversos na saúde humana, nomeadamente erupção cutânea, taquicardia, náuseas, dores de cabeça e problemas gastrointestinais. Por esta razão, a determinação de histamina tornou-se um dos principais parâmetros de controlo de qualidade de alguns alimentos [1]. A determinação do teor de histamina em alimentos é geralmente realizada por cromatografia líquida de alta eficiência (HPLC) que, apesar de serem métodos eficientes e fiáveis, exigem processos de extração demorados e trabalhosos e requerem instrumentação cara e sofisticada, normalmente manuseados por operadores altamente treinados e qualificados. Metodologias baseadas em fotoluminescência (PL) têm atraído grande atenção devido à crescente necessidade de realizar ensaios de rastreio mais simples, rápidos e no local para monitoramento de substâncias tóxicas em alimentos. Nesse sentido, o uso de pontos quânticos (QDs) como elementos sensores de PL pode ser encarado como uma opção valiosa tendo em vista as suas notáveis propriedades óticas [2].

Neste trabalho foi realizado o estudo cinético da interação entre a histamina com pontos quânticos ternários de $AgInS_2$ passivados com ácido 3-mercaptopropiónico (MPA-AIS QDs) e com pontos quânticos de carbono (CDs). Tendo em conta os resultados obtidos, foi desenvolvida uma sonda raciométrica combinando CDs (emissão a 506 nm, fluoróforo de referência) e MPA-AIS QDs (emissão a 744 nm, fluoróforo modulado pela histamina). Na sonda raciométrica desenvolvida verificou-se a inibição da intensidade de PL de MPA-AIS QDs enquanto que a intensidade de emissão dos CDs permaneceu praticamente inalterada, devido à sua inércia química em relação ao alergénio. Com o objetivo de desenvolver uma metodologia analítica para a deteção e quantificação da histamina em amostras alimentares, foi estudada rigorosamente a cinética do processo de interação entre a sonda raciométrica e o alergénio. Os dados obtidos referentes à evolução ao longo do tempo dos espectros de emissão da sonda raciométrica na presença do analito podem ser considerados como dados instrumentais de segunda ordem, os quais foram analisados por modelos quimiométricos multivariados de segunda ordem, nomeadamente, U-PLS (*unfolded- partial least squares*) e ANN (*artificial neural network*). Assim foi possível obter a vantagem de segunda ordem, o que significa que a histamina pode ser detetada e quantificada mesmo na presença de espécies interferentes na matriz da amostra sem que esses interferentes tenham sido calibrados. A abordagem cinética proposta com auxílio dos modelos matemáticos permite reduzir o limite de deteção e melhorar a sensibilidade e seletividade.

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Potential inhibitory effect of new xanthones on acetylcholinesterase: an automatic assay

Thierno Moussa Ndongo [1, 2], Fernando Durães [3, 4], Diana Resende [3, 4], Madalena Pinto [3, 4], Emília Sousa [3, 4], M. Lúcia M. F. S. Saraiva[1], Marieta L. C. Passos [1,*]

[1]LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, Porto University, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[2]Faculté des sciences et techniques, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans cedex 9, France
[3]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[4]Centro Inter. Invest. Marinha e Ambiental (CIIMAR/CIMAR), Universidade do Porto, Edif. Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal
**marietapassos@gmail.com*

Alzheimer´s disease is a neurodegenerative disorder with a high incidence rate [1]. It is related with the reduced concentration of the neurotransmitter acetylcholine at the cholinergic synapsis, promoted by the enzyme acetylcholinesterase activity [2]. Thus, the current therapy is based on the use of acetylcholinesterase inhibitors. Xanthones were described by some of us as potential anti-Alzheimer agents [3].

In this work, new aminated (thio)xanthones were synthetized and their inhibitory effect on the acetylcholinesterase enzyme was evaluated. The synthesis of aminated xanthones was performed as previously described [4]. Aminated thioxanthones have been prepared through a copper-catalyzed Ullmann type C – N coupling. In order to perform the study, it was implemented the Ellman's reaction [5] in an automatic µSIA-LOV system [6] and chemical and physical parameters were studied to promote the best performance. Docking studies in acetylcholinesterase (PDB: 4ey7) were also performed in order to clarify the potential interaction sites between the hit compounds and the target.

It was verified that depending on the structure of the molecules, some of the new xanthones present a great potential to be used in the Alzheimer's disease treatment. For four of them, (EC_{50}) values between 676 and 4466 µmol L-1 were calculated, showing a higher inhibitory effect than rivastigmine, a known inhibitory drug usually used in the treatment of this disease.

The developed µSIA-LOV showed to be a simple, rapid, robust and reliable automatic alternative to perform the inhibitory studies. It also allowed the reduction of reagents and sample consumption (around 55 µL per analysis), the cost per analysis and the waste generation (around 1.2 mL per analysis), being in accordance with the principles of green analytical chemistry.

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Development of a microfluidic paper-based analytical device for the determination of iodide

Mafalda G. Pereira, António O.S.S. Rangel, Raquel B.R. Mesquita*

Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 137, 4169-005, Porto, Portugal
** rmesquita@ucp.pt*

Iodine is an oligoelement fundamental to produce the thyroid hormones, which makes it a key parameter to assess the health condition. The iodine intake will affect the fetal development and the regulation of the cell's metabolic activities as well as appropriate growth and development. When iodine levels are deficient, the synthesis of the thyroid hormones is diminished, causing development and functional abnormalities, also known as iodine deficiency disorders. The most common are goitre and swelling of the thyroid gland both in children and adult. Additionally, iodine deficiency during early childhood can cause irreversible deficits in cognitive development and during pregnancy it can lead to fetal death or cretinism, causing severe retardation both in mental and physical growth [1].

The World Health Organization (WHO) estimates that 285 million children and nearly 2 billion individuals worldwide have insufficient iodine intake, being different geographic areas susceptible to different levels of iodine intake deficiency it is considered a public health problem in more than 50 countries. Trying to prevent the previously mentioned iodine deficiency disorders, the WHO as well as the United Nations Children's Fund (UNICEF) and the International Council for the Control of Iodine Deficiency Disorders Global Network (ICCIDD) promote salt iodization. This approach was easily adopted due to the widely consume of salt by all population groups, the inexpensiveness and well established technologies for the iodization process together with a wide consumer acceptability, as none of the salt's properties are affected [1]. In spite of the benefits, there is also concern that due to population's efforts to reduce salt intake because of elevated blood pressure and hypertension, there may be an increase in iodine deficiency disorders.

In this work, we propose to develop a microfluidic paper-based analytical device (µPAD) to quantify the iodide in salt and iodized salt. A µPAD is a small microfluidic device that presents itself quite relevant in terms of its analytical capacity. It consists of a hydrophilic zone to carry out the chemical reaction, and an hydrophobic zone to be the physical barrier of the reaction. These devices can be produced in different ways and adapted to the target reaction and quantifications [2]. To quantify the iodide present in the sample, the reaction between iodide, peroxide and 3,3',5,5'-tetramethylbenzidine (TMB) was chosen, in which I^- catalyzes TMB to its blue oxidized form, in the presence of H_2O_2 [3].

Being the µPAD easily disposable, low-cost and user friendly, it represents a valuable tool for point-of-care analysis [2] and can be used by untrained personal at home.

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Characterization of *Achillea mellefolium* flower extracts as ingredients in organic cosmetics

L. Rubio[1,2,*], M.J. Expósito[3,4], M.C. Valiño[3,4], C. Garcia-Jares[1,2], M. Lores[2]

[1]CRETUS, [2]Laboratory of Research and Development of Analytical Solutions (LIDSA), Department of Analytical Chemistry, Nutrition and Food Science, University of Santiago de Compostela. Avda. das Ciencias s/n, E-15782, Santiago de Compostela, Spain
[3]Milhulloa S.Coop.Galega, Lugar Coto 1, E-27204, Palas de Rei, Lugo, Spain
[4]Cosmética Muuhlloa SL., Lugar de Cumbraos 1, E-27215, Monterroso, Lugo, Spain
* *laura.rubio.lareu@usc.es*

Plants are a source of botanical ingredients with outstanding properties for application in cosmetic formulations based on their traditional use [1]. An interesting approach towards this use involves the revaluation of co-products and by-products generated in the commercial exploitation of various plants in the agriculture, food, and forestry sectors. Other strategies involve previously cultivated plants as spices or infusions, or even other wild ones. This is an innovative concept that gives extra value and facilitates the approach to a circular economy.

Among the typical Galician organically cultivated botanicals considered, this study covered dried flowers of Yarrow plant (*Achillea mellefolium*). It is important to note that some phytochemical profiles were not yet analytically characterized in depth. Some plants are completely unexplored or not studied at species level. Extracts from these plants contain polyphenols among other valuable bioactive compounds. To extract these substances, we propose a simple and rapid procedure based on ultrasound-assisted extraction (UAE) with green solvents in order to improve the yield and exploitation possibilities of the extracts obtained, by comparing them with alcoholates and hydrolates obtained in the classical way. After suitable dilution, if necessary, all samples were injected directly. The subsequent analysis by liquid chromatography-tandem mass spectrometry (LC-MS/MS) allowed knowing the polyphenolic profile, identifying a total of 16 polyphenols including both common and more specific ones.

The most remarkable properties of the identified phytochemicals are their antioxidant capacity, intense antimicrobial activity, and the existence of evidence of other beneficial properties for the skin [2,3], enabling them to be used as valuable and multifunctional ingredients in original and organic cosmetics that will respond to the current demands of society.

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UPLC-MS lipidomic approach to evaluate potential biomarkers for the differentiation of HIV/HCV progressive stage

K.Tkachenko, I. Arenzana Rámila, J-M Gonzalez-Saiz, T. Mehany, C.Pizarro*

University of La Rioja, calle Madre de Dios 53, Logroño, Spain
**consuelo.pizarro@unirioja.es*

Human immunodeficiency virus (HIV) and Hepatitis C virus (HCV) have been diagnosed in millions of people worldwide with very high mortality rates and, on the other hand, has a very pronounced impact on the quality of life of HIV-positive patients [1]. In addition, the disease mechanisms have remained poorly understood for a long time. Thus, tardive intervention in the diagnosis, prevention, control and treatment of viral outbreaks has accompanied the growth and spread of this disease.

Antiretroviral treatments used to reduce the plasma viral load of HIV and HCV viruses are capable of causing drastic changes in lipids, causing alteration of the lipid metabolism of the infected organism and developing diseases such as dyslipidaemia, hypertriglyceridemia, hypercholesterolemia and insulin resistance, among other diseases [2-4].

This study aimed to identify altered lipid levels in plasma samples from HIV-infected patients with different stages of infection and co-infection with HCV using the analytical platform UPLC-MS. At the same time, the results obtained allowed us to suggest and establish possible biomarkers of the diseases analysed. The cohort groups were selected based on the stage of the disease: i) asymptomatic patients infected with HIV (21); ii) patients infected with HIV who had developed AIDS (11); iii) nine patients infected with HIV and co-infected with hepatitis C (HIV/HCV); iv)13 patients with AIDS and co-infected with HCV (AIDS/HCV) and v) 20 control subjects (Control).

The results obtained with the UPLC-MS platform, the multivariate analysis of chromatograms and the study of discriminant lipids through ROC curves have allowed the discovery of lipid alterations in patients with different stages of HIV and co-infected with HCV. Among the lipid families that showed the most significant discriminating power to differentiate the different stages of the disease, triglycerides and phosphatidylcholines stood out since they underwent significant changes in their concentrations. For this reason, the key biomarkers of the diseases studied are these two families. However, using other lipid families that, in combination, act as biomarkers is required to define each disease more precisely and the differences between them. Therefore, this study should be considered a reasonable basis for future studies where a more significant number of samples are included and analysed.

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Ion mobility spectrometry for the rapid and simultaneous analysis of three common analgesics

C.Pizarro, K.Tkachenko, J-M González-Saiz

University of La Rioja, C/ Madre de Dios 53, Logroño (La Rioja), Spain
**consuelo.pizarro@unirioja.es*

Currently, routine analytical laboratories are required to analyse many samples daily, so the analytical techniques must be fast and accurate [1]. Ion Mobility Spectrometry (IMS) is an alternative to the conventional techniques currently used in routine analytical laboratories. This technique allows for obtaining qualitative and quantitative information on ionisable compounds present in drugs, which facilitates the immediacy of the results and the measurements' accuracy at a low cost [2].

This work describes a new approach for the rapid analysis of active ingredients (caffeine, paracetamol and acetylsalicylic acid), a widely used pharmaceutical combination with analgesic effects.

The factors influencing ion mobility spectrometry (IMS): ionisation source voltage, drift tube voltage, ionisation source temperature, drift tube temperature, drift tube flow and exhaust pump flow have been tuned and optimised using experimental design methodology [3]. By applying desirability functions, optimal compromise conditions were established for simultaneously determining the active substances under study: caffeine, paracetamol and acetylsalicylic acid. The optimal values for the variables in the determination of these compounds were: ionisation source voltage, 2287 V; drift tube voltage, 8000 V; ionisation source temperature, 160ºC; drift tube temperature, 170ºC; drift tube flow rate, 1.28 L/min and exhaust pump flow rate, 0.67 L/min.

Once the method was optimised, it was validated by analysing the linearity, limits of detection and quantification, sensitivity, reproducibility and repeatability. For this purpose, different solutions of the three analytes were used in methanol: water solution (80:20) in a range of concentrations from 0.4-12 ppm for caffeine and paracetamol and from 5-102 ppm for acetylsalicylic acid.

The developed method was applied to an actual sample with excellent results opening up its potential application in quality control analysis in production.

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Partículas de caucho procedentes de ruedas de coche: determinación de agentes químicos relacionados con la mortalidad de especies acuáticas

Andrés Duque-Villaverde[1]*, Daniel Armada[1], María Celeiro[1], Thierry Dagnac[2], María Llompart[1]

[1] CRETUS, Departamento de Química Analítica, Nutrición y Bromatología, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, España.
[2] Centro de Investigaciones Agrarias de Mabegondo (AGACAL-CIAM), Unidad de Contaminantes Orgánicos, Apartado 10, E-15080, A Coruña, España.
**andres.duque@rai.usc.es*

El caucho de los neumáticos contiene una gran cantidad de agentes químicos que se añaden para aportarle resistencia y durabilidad. Algunos de estos compuestos son preocupantes debido a su entrada en el medioambiente mediante las partículas de desgaste de neumáticos, consideradas un microplástico, y el caucho reciclado empleado en campos de césped artificial y en parques infantiles [1,2]. Entre las sustancias de estudio se encuentran, entre otros, el antiozonante 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine) a partir del que se puede formar como producto de degradación la 6PPDq (N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine-quinone), cuya presencia en el medio acuático parece estar asociada con la mortalidad del salmón coho en el noroeste del Pacífico [3]. Otros agentes químicos de interés por sus implicaciones medioambientales, además de sus efectos en la salud humana, son los aditivos vulcanizantes y reticulantes [4,5].

Por lo tanto, el objetivo de este trabajo es el desarrollo de una metodología analítica para la detección simultánea de estos agentes basada en la extracción asistida por ultrasonidos (UAE), seguida de cromatografía líquida acoplada a espectrometría de masas en tándem (LC-MS/MS). Para ello, se han optimizado parámetros que afectan a la eficacia de la extracción como el disolvente y la temperatura. Finalmente, el método se ha validado y aplicado a diversas muestras de caucho de neumático reciclado procedentes de campos de fútbol y parques infantiles, principalmente de Galicia, demostrando la presencia de estos agentes químicos en muchas de ellas, incluyendo la 6PPDq. En definitiva, este tipo de superficies pueden constituir una de las fuentes principales de entrada de estos compuestos en el medioambiente, incluyendo los ecosistemas acuáticos.

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DESENVOLVEMENTO DUN MÉTODO ANALÍTICO BASEADO NA EXTRACCIÓN ASISTIDA POR ULTRASÓNS SEGUIDO DE CROMATOGRAFÍA LÍQUIDA ACOPLADA A ESPECTROMETRÍA DE MASAS EN TÁNDEM PARA A DETERMINACIÓN DE HERBICIDAS EN SOLOS

Castiñeira-Landeira, Ana[1,*]; Vazquez, Lua[1]; Gonzalez-Leirado Helena[1]; Dagnac, Thierry[2]; Llompart, María[1]

[1]CRETUS, Departamento de Química Analítica, Nutrición e Bromatoloxía, Universidade de Santiago de Compostela, E-15872, Santiago de Compostela, España.
[2]Axencia Galega de Calidade Alimentaria – Centros de Investigación Agrarias Mabegondo (AGACAL-CIAM) – Unidade de contaminantes orgánicos, apartado 10, E-15080, A Coruña, España.
*ana.castineira.landeira@rai.usc.es

Os herbicidas son un tipo de pesticidas que se empregan coa finalidade de interromper ou inhibir o crecemento de plantas non desexadas en cultivos que son ou serán cultivados. A súa necesidade xurde da gran demanda de productos agroalimentaria para a sustentabilidade da poboación. Pola contra, algúns dos produtos químicos poden ser tóxicos e contaminantes [1], persistindo en solos e cuxos residuos poden alcanzar facilmente diferentes ecosistemas acuáticos a través da lixiviación en solos de cultivo. Unha alternativa para reducir a dose de herbicidas en solo é o emprego de emendas orgánicas como o biocarbón (material vexetal procedente da pirólise) que pode axudar a previr e a remediar a contaminación do solo e auga [2].

O obxetivo deste traballo é o desenvolvemento e validación dun método analítico verde, simple e rápido para identificar e cuantificar a presenza de herbicias en mostras de solo mediante cromatografía líquida acoprada a espectrometría de masas en tándem (LC-MS/MS). En primeiro lugar, leváronse a cabo probas preliminares nas que se estudaron e compararon dúas técnicas de extracción (extracción asistida por ultrasóns e extracción por vórtex), tres disolventes (ou mezcla de disolventes) de extracción (metanol, acetonitrilo e mezcla de fase acuosa/fase orgánica H_2O:MeOH 40:60) e o emprego de solos con ou sen emenda orgánica. Optimizáronse outros parámetros que tamén poden afectar á eficiencia da extracción asistida por ultrasóns (UAE) mediante un deseño experimental que inclúe como factores: a porcentaxe de metanol no disolvente de extracción, o volumen do disolvente, a cantidade de mostra de solo e o tempo de extracción. Ademais, comparáronse a UAE e a extracción asistida por microondas (MAE), así como a temperatura de extracción. En condicións óptimas, o método UAE-LC-MS/MS foi validado para 10 herbicidas mostrando resultados satisfactorios en termos de linearidade ($R^2>0,9988$), exactitude, obtención de recuperacións cuantitativas (en torno ao 100% en tódolos casos) e precisión, revelando valores de desviación estándar relativa (RSD) inferiores ao 10%. Finalmente, o método aplicouse a mostras reais de solos de cultivos de Galicia. A metodoloxía proposta é simple, rápida, de baixo custo e de fácil aplicación en calquera laboratorio cumprindo os obxectivos da química verde e os criterios de sustentabilidade.

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Estimación del comportamiento en frío del biodiesel

M.C. Fernández-Feal[1*], **Paola Escudero-Rivera, J.R. Pérez-Prado**

[1]CONTROLQ_LABCOMB-UDC (BIOENGIN), CITENI-Campus Industrial, Ferrol (a Coruña), España
**coro.ffeal@udc.es*

El biodiesel tiene ventajas significativas sobre el diesel: mayor lubricidad, mayor punto de inflamación, baja toxicidad, cantidades insignificantes de azufre, biodegradabilidad y menos emisiones a la atmósfera. Sin embargo, al mismo tiempo, también tiene importantes desventajas: menor estabilidad a la oxidación, contenido energético reducido y problemas de comportamiento en frío. Entre estas propiedades, cobra especial relevancia el comportamiento en frío, que se determina mediante el POFF (Punto de obstrucción de filtros en frío); en los motores de encendido por compresión, el valor de POFF está limitado por especificación legal.

La relación entre las características de la materia prima utilizada y las propiedades en frío del biodiesel obtenido como producto final, se convierte en el primer paso en el desarrollo de un modelo matemático que permita la predicción del valor del POFF y posibilite optimizar el diseño del proceso para la producción de biodiesel en planta.

El estudio se ha realizado sobre los tres tipos de aceite más utilizados en la planta de biodiesel de referencia en el estudio: soja, palma y colza.

Las muestras de aceite se caracterizaron mediante el análisis de parámetros fisicoquímicos: humedad, acidez, índice de yodo, materia insaponificable… y el análisis mediante cromatografía gaseosa. Además, se evaluaron y estudiaron diferentes métodos para encontrar el más cercano al proceso de producción de ésteres metílicos a escala industrial.

Mediante el análisis de las propiedades de los aceites y del biodiesel obtenido a partir de los mismos se estudiaron diferentes relaciones de dependencia, facilitando la posterior obtención de modelos predictivos en base a la:

- correlación entre el porcentaje de ésteres saturados y POFF.
- correlación entre el porcentaje de aceite utilizado y POFF.

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Dilución por biocombustible del aceite lubricante

M.C. Fernández-Feal[*,1], **J.R. Pérez-Prado**[1], **B. Sánchez-Fernández**[1]

[1]CONTROLQ_LABCOMB-UDC (BIOENGIN), CITENI-Campus Industrial, Ferrol (a Coruña), España
**coro.ffeal@udc.es*

La contaminación por combustible del aceite lubricante en un motor, consecuencia de que parte del combustible introducido en la cámara de combustión no se queme y descienda hacia el cárter a través de la falda del pistón, origina graves problemas en el sistema de lubricación por lavado del lubricante en puntos clave del sistema de lubricación y modificaciones significativas en determinadas propiedades (viscosidad, punto de inflamación) determinantes para asegurar la correcta funcionalidad del aceite lubricante en el sistema.

La presencia de biocombustible (FAME) en los combustibles utilizados como carburantes presenta un reto añadido para los lubricantes. Las altas temperaturas a las que se ve sometido el aceite en el cárter favorecen la evaporación de las fracciones más volátiles del carburante diluido en él, mientras que las más pesadas permanecen: se va concentrando una mayor cantidad de FAME en el aceite que al ser menos volátil y más viscoso provoca un espesamiento del lubricante provocando que circule con mayor dificultad a través del circuito de lubricación del motor. Los fenómenos relacionados con el biocombustible son tan importantes, que la asociación de fabricantes de vehículos europeos, ACEA, ha desarrollado ensayos específicos al respecto.

Un lubricante de calidad contrastada, correctamente formulado, debe de ser capaz de soportar no solo la posible dilución por combustible, sino también los efectos adversos de los biocombustibles en el aceite de motor.

El presente trabajo estudia las variaciones sufridas por la viscosidad cinemática y el punto de inflamación de un aceite lubricante comercial, ACEA E7, a consecuencia de sufrir una dilución por combustible conteniendo FAME.

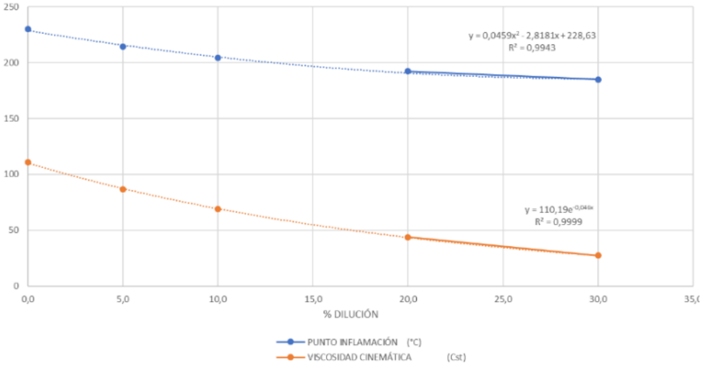

Fig.1. Viscosidad cinemática y punto de inflamación / %dilución por combustible

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Evaluation of the Phenolic Content of Galician Honeys to Identify their Botanical Origin

Lua Vazquez[1,*], Daniel Armada[1], Maria Celeiro[1], Thierry Dagnac[2], Maria Llompart[1]

[1]CRETUS, Department of Analytical Chemistry, Nutrition and Food Science, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain
[2]Galician Agency for Food Quality-Agronomic and Agrarian Research Centre (AGACAL-CIAM), Unit of Food and Feed Safety and Organic Contaminants, Apartado 10, E-15080 A Coruña, Spain
*lua.vazquez.ferreiro@usc.es

Honey is a natural product well known for its beneficial properties. It is mainly composed by sugars, especially fructose and glucose, and water, but other minor component as minerals, proteins, enzymes, vitamins and other numerous valuable substances are also present [1]. The antioxidant properties of honey are attributed to its phenolic compound content, and they depend on the botanical origin, but also on other factors such as the climate or the processing. Thus, phenolic compounds are deemed potentially useful markers for the characterization of honey, the determination of its botanical and/or geographical origin, the quality of honey and the nutraceutical value [2].

In this context, the main objective of this work is the development of a simple, miniaturized and environmentally friendly methodology to determine 42 phenolic compounds in Galician honeys (Northwest Spain) from different honey varieties (chestnut, eucalyptus, blackberry, heather and multi-floral). For that, the method based on vortex extraction (VE) and ultrasound assisted extraction (UAE) followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) was optimized and was validated in terms of linearity, precision and accuracy, obtaining satisfactory results. In addition, the total phenolic content (TPC) and antioxidant activity (AA) were also evaluated.

Finally, the VE-UAE-LC-MS/MS methodology was applied to the real samples, showing the presence of 25 phenolic compounds in the 91 analyzed samples, reaching concentrations up to 252 µg g^{-1}. Statistical tools such as analysis of variance (ANOVA) and principal component analysis (PCA) were employed in order to classify the different honeys according to their botanical origin. The TPC, AA and ∑phenolic compounds showed significant differences appeared depending on the honey variety, being several of the identified phenolic compounds responsible of the main differentiation.

Acknowledgments
This research was funded by project GO FEADER 2018/054B (Xunta de Galicia). The authors belong to the National Network for the Innovation in miniaturized sample preparation techniques, RED2018-102522-T (Ministry of Science, Innovation and Universities, Spain), and to the Galician Competitive Research Groups IN607B 2019/13 and ED431 2020/06 (Xunta de Galicia). This study is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. All these programmes are co-funded by FEDER (EU).

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Electrochemical determination of cholecalciferol in water-ethanol mixtures using a glassy carbon electrode and unmodified screen-printed carbon electrodes

Fátima Daniela Gonçalves, José António Rodrigues, Rui Miguel Ramos*

LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre s/n, Porto, 4169-007, Portugal
**rui.ramos@fc.up.pt*

Vitamin D, one of the many nutrients essential for the body's normal functioning, can mainly be found in two forms: ergocalciferol (vitamin D_2), found in plants and acquired through ingestion, or cholecalciferol (vitamin D_3), produced by the body when exposed to sunlight [1]. Vitamin D deficiency has a direct influence on the absorption of calcium and phosphorus in the body, while low levels are known to cause symptoms of various diseases such as cancer, cardiovascular disease, and immunological abnormalities [2].

In this work, an electrochemical method was developed and optimised in order to determine vitamin D_3 based on its irreversible oxidation at +1,2 V (vs. Ag/AgCl, 3 mol L^{-1} KCl). For such, a glassy carbon electrode (GCE) and a platinum electrode, as working and auxiliary electrodes, respectively, completed the three-electrode system. Furthermore, unmodified screen-printed carbon electrodes (SPCE) were also used.

Cyclic voltammetric studies carried out on the GCE led to conclude that the optimised electrolyte solution was of equal parts water:ethanol (1:1) and 0,100 mol L^{-1} of lithium perchlorate. Square wave voltammetry was the most suitable voltammetric method for vitamin D_3 determination, when the amplitude is 50 mV, the potential step is 5 mV and the frequency is 50 Hz. This method showed to be precise and had a linear response under constant stirring between 1,40 and 123 µmol L^{-1} of cholecalciferol. The method was also adapted and optimised for unmodified screen-printed carbon electrodes (SPCE), where it showed to be precise with a linear response when using different drops of sample on the same electrode. The optimised method was then applied on commercial tablets of vitamin D_3.

Funding

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Acknowledgements

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Exploring the emission of volatile carbonyl compounds from wood-based panels by GDME and HPLC-DAD-MS/MS

Fátima Daniela Gonçalves, José António Rodrigues, Rui Miguel Ramos*

LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, Rua do Campo Alegre s/n, Porto, 4169-007, Portugal
**rui.ramos@fc.up.pt*

Wood-based panels (WBPs) is a general term used for different board products made with fibres, particles, or veneers, which includes particleboards, medium-density fibreboards, oriented stand boards, and others. All of them share similar characteristics: an adhesive (thermosetting resin) is combined with particles or fibres to create a wood-adhesive matrix that, by means of heat and/or pressure in a press, bonds the particles to form a solid panel. Its demand is increasing as a result of being a cheap building material together with the rising cost of wood. The emission of volatile organic compounds (VOCs) from WBPs and their influence on the quality of the indoor air is a topic of interest among different European agencies, due to the increasing periods of time spent indoors and the possible impacts of these compounds on human health [1].

Gas-diffusion microextraction (GDME) [2,3] is a technique that consists on the extraction of volatile analytes through a permeable membrane to an acceptor solution (containing a derivatization reagent). GDME is a faster, simpler, and cheaper alternative method for the determination of carbonyl compounds, when compared to commonly applied methods, as it allows for the simultaneous isolation, concentration, and derivatization of the analytes.

In this work, GDME was used for the extraction of carbonyl compounds directly from WBPs without any sample pre-treatment. Different extraction parameters were studied and optimized, such as the influence of the temperature, time, sample mass, volume of acceptor solution, among others. The choice of derivatization reagent was also evaluated, between 2,4-dinitrophenylhydrazine and 4-hydrazinobenzoic acid, as well as their concentration. HPLC-DAD and HPLC-DAD-MS/MS studies were performed on the extracts of particleboards and medium-density fibreboards with different characteristics and production processes.

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QUÍMICA FÍSICA

Localization and interaction of 3-hydroxy-4-pyridinone chelators with DMPC model membranes: A DSC and EPR Study

Luísa M.P.F.Amaral[1,*], **Tânia Moniz**[1,2], **Maria Rangel**[2]

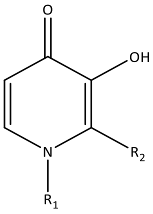
[1]REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. do Campo Alegre, 4169-007, Porto, Portugal
[2]REQUIMTE, LAQV,Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
**luisaamaral@fc.up.pt*

The class of 3-hydroxy-4-pyridinone (HPOs) chelators is widely known and valuable for biomedical and pharmaceutical purposes. Their chelating properties towards biologically-relevant transition metal ions highlight their potential biomedical utility. Indeed, HPOs form outstanding building blocks for the development of a variety of agents in the field of metal chelation. Moreover, the hydrophilic/lipophilic balance of ligands and complexes can be tuned by variation of substituents on the heterocyclic ring without altering the stability of the complexes [1]. This latter property is crucial to design molecules with the appropriate permeation properties across membranes. The knowledge of the permeation properties across lipid bilayers is relevant to understand the mechanism of action of drugs and a significant contribution to the development of new bioactive compounds.

In the present study we discuss the interaction of seven 3-hydroxy-4-pyridinone chelators (Table.1), of different lipophilicities, with 1,2-Dimyristoyl-sn-glycero-3-phosphocholine, (DMPC), unilamellar liposomes. In a recent study, Molecular Dynamics simulations suggest that the ligand with the highest partition to the bilayer is Hhexylmpp, with at least two orders of magnitude higher K_{mem} when compared to the other ligands [2]. To explore and validate the theoretical results, an experimental biophysical study was performed, using differential scanning calorimetry (DSC) and electron paramagnetic resonance spectroscopy (EPR), to investigate the molecular interactions between HPOs ligands and DMPC, liposomes as model cell membranes.

The results corroborate previous Molecular Dynamics simulations, showing that increasing the length of the alkyl chain in the R_1 substituent is important for the ability of the chelator to diffuse through the lipid bilayer.

Table 1. Formulas and abbreviation of 3-hydroxy-4-pyridinone chelators.

	Ligand	**R_1**	**R_2**
	Hmpp	H	CH_3
	Hdmpp	CH_3	CH_3
	Hdetpp	CH_2CH_3	CH_2CH_3
	Hetmpp	CH_2CH_3	CH_3
	Hbutmpp	$(CH_2)_3CH_3$	CH_3
	Hmeetmpp	$(CH_2)_2OCH_3$	CH_3
	Hhexylmpp	$(CH_2)_5CH_3$	CH_3

Acknowledgments This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020. L.M.P.F. Amaral thanks FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018 (CEECIND/03202/2018).

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QF14

The effects of DMSO on the thermal properties of DMPC liposomes

Luísa M.P.F.Amaral[1,*], Maria Rangel[2], Margarida Bastos[3]

[1]REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. do Campo Alegre, 4169-007, Porto, Portugal
[2]REQUIMTE, LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[3]CIQ-UP, Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. do Campo Alegre, 4169-007, Porto, Portugal
**luisaamaral@fc.up.pt*

To study drug-membrane interactions, it is crucial to dissolve the drug and prevent precipitation during the experiments. However, many drug candidates are poorly soluble in water, and therefore it is often necessary to use a co-solvent to improve dissolution capacity, with DMSO being the most commonly used solvent for pharmaceutical drugs. Nevertheless, its effect on phospholipid membranes is not fully addressed and still raises some questions.

In this work, a comparative study has been made on the influence of DMSO on fully hydrated DMPC liposomes, in a concentration range of 0 - 40% (v/v), by Differential Scanning Calorimetry (DSC). Our results show that the effect of DMSO depends on concentration and sample preparation method. For LUVs and MLUVs, where DMSO is added to the liposome suspension after preparation, with low DMSO < 10% (v/v), little or no change is observed in the liposome suspension thermal properties. With higher DMSO concentrations, (10% < DMSO < 40%) there is a gradual increase in the transition temperature (T_m), a decrease in transition cooperativity ($\Delta T_{1/2}$ increases) and a decrease in transition enthalpy (ΔH). For MLUVs, an increase in the pre-transition temperature is also observed, until it disappears for DMSO at 40%.

For MLUVs prepared from lipid film hydration using various DMSO/water concentrations in film hydration, the main effect was an increase in transition and pre-transition temperatures, along with a small decrease in ΔH values and no change in main transition cooperativity.

To further test the DMSO influence on drug permeation properties, in the range (0 < DMSO < 10%), a series of experiments were performed using two Sodium Dodecyl Sulphate concentrations and varying DMSO content for each one. It was found that although DMSO up to 10% did not change significantly the thermal properties of DMPC liposomes, for DMSO content from 7% the partitioning behaviour of the drug is affected.

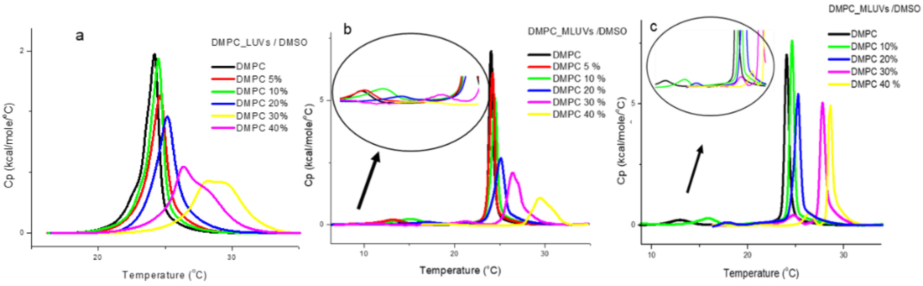

Fig.1. The DSC heating thermograms of DMPC liposomes with different percentages of DMSO (V/V); a) LUV´s (incubation); b) MLUVs, (incubation); c) MLUVs, (incorporation)

Acknowledgments This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020. L.M.P.F. Amaral thanks FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018 (CEECIND/03202/2018).

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Caracterización fotofísica da interacción do 6-amino-2-ciano-1,3-benzotiazol con proteínas amiloides e seroalbumina humana e bovina

Diego Cora[1,*], Ana Arias Rodríguez[1], Adrián Hervés Pardavila[1], Mercedes Novo[2] e Flor Rodríguez Prieto[1,*]

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Departamento de Química Física, Universidade de Santiago
de Compostela, 15782 Santiago de Compostela, España
[2]Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela, E-27002 Lugo, España
**diego.cora@rai.usc.es e flor.rodriguez.prieto@usc.es*

O 6-amino-2-ciano-1,3-benzotiazol (ACB) é unha sonda fluorescente sensible á polaridade do microentorno, químico ou biolóxico no que se atope. Isto faino un bo candidato para a cuantificación de proteínas de interese, como a seroalbumina bovina e humana e proteínas amiloides, formadas por 40 ou 42 aminoácidos, en distintos graos de agregación. Estas últimas proteínas están relacionadas coa orixe de enfermidades dexenerativas como o Alzhéimer [1]. É de gran interese o deseño de sondas fluorescentes sensibles á presenza e á agregación destas proteínas. Así mesmo, a asociación entre as seroalbuminas e as proteínas amiloides constitúe a base de novos tratamentos do Alzhéimer por intercambio plasmático [2], en fase de estudos clínicos, polo que a cuantificación das seroalbuminas a través de sondas fluorescentes tamén é relevante.

O obxectivo deste traballo é a caracterización da interacción da sonda fluorescente ACB coas seroalbúminas humana e bovina, e coas proteínas amiloides en distintos graos de agregación, para a súa posible cuantificación. Para iso utilizáronse técnicas fluorescentes en estado estacionario e anisotropía, e fluorescencia resolta no tempo.

Os nosos resultados indican unha forte interacción entre a sonda e as seroalbuminas humana e bovina, permitindo a cuantificación da proteína en disolución. En cambio, a interacción coas proteínas amiloides é menos efectiva.

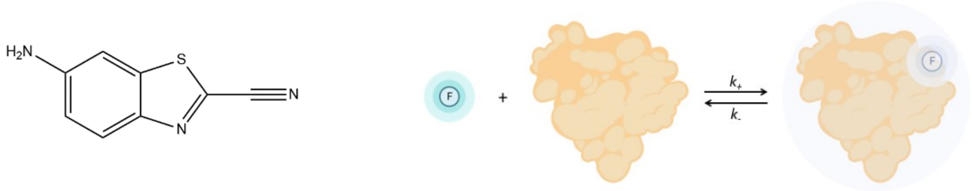

Fig.1. Estrutura molecular do 6-amino-2-ciano-1,3-benzotiazol e representación gráfica dunha sonda fluorescente uníndose a unha proteína xenérica.

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Thermal and photochemical reactions of n-pyridinechalcones (n= 2’, 3’, 4’)

Ambrósio Camuenho[1,*], **A. Jorge Parola**[1], **Alfonso Alejo-Armijo**[1], **César A. T. Laia**[1], **Fernando Pina**[1]

[1] LAQV-REQUIMTE, FCT - Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal.
**email: a.camuenho@campus.fct.unl.pt*

The kinetics and thermodynamics of the pH-dependent equilibrium network of species (multistate) generated by trans-2’-pyridinechalcone, trans-3’-pyridinechalcone and, trans-7-diethylamino-4’-pyridinechalcone [1] were studied by UV-vis spectroscopy, 1H NMR, and HPLC/MS. Due to the slow kinetics of the multistate species interconversion, the conjugation of these techniques has shown to be a powerful tool for the investigation of these systems. The species present in the multistate change with the position of pyridine nitrogen and with the introduction of an amino group. The results are compared with those reported for 4’-pyridinechalcone [2], 7-diethylamino-4’-hydroxyflavylium [3] and 2’-hydroxychalcone[4]. While 3’-pyridinechalcone has a multistate similar to that of 4’-pyridinechalcone [2], the multistate of 2’-pyridinechalcone contains two new products. On the other hand, introduction of an amino group in position 7 to yield 7-diethylamino-4’-pyridinechalcone [1] allows formation of the respective (pseudo)flavylium, 7-diethylamino-4’-pyridine-1-benzopyrylium (Figure1). Pyridinechalcones and their multistates have potential biological applications [5,6].

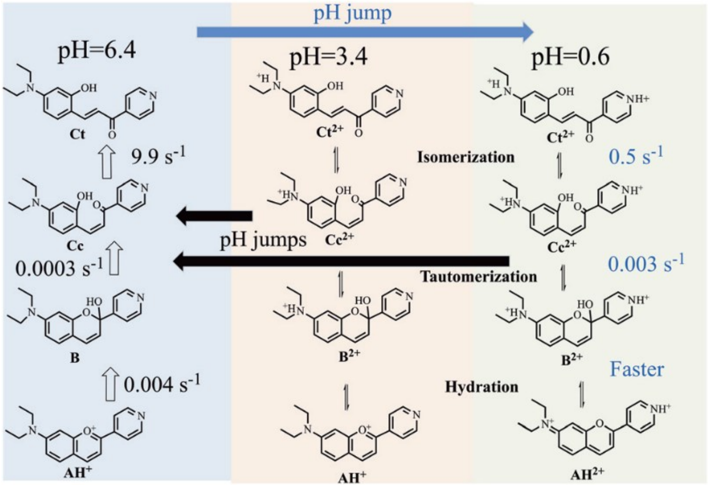

Figure 1: Summary of the multistate composition of 7-diethylamino-4’-pyridinechalcone and conversion rates at pH 0.6, 3.4 and 6.4 [1].

Acknowledgments
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iSenseDSC: a high precision microcalorimeter

Rodrigo M. A. Silva[*], **Ana I. M. C. Lobo Ferreira, Luís M. N. B. F. Santos**

CIQUP, Institute of Molecular Sciences (IMS) – Department of Chemistry and Biochemistry, Faculty of Sciences,
University of Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
** rodrigo.m.a.silva98@gmail.com*

This work presents the refurbishment, upgrading and testing of a differential scanning microcalorimeter. With the aim of improving its temperature stability and signal resolution, several changes were made to the original apparatus (SETARAM micro DSC III). The original heat pumping and exchanging system was replaced by a more modern and efficient system (produced by Laird Thermal Systems). The location of the temperature control point was changed, and a temperature control module was built. Furthermore, the overall insulation of the calorimeter was reinforced and a new pre-amplification system (originally developed in the former Thermochemistry Laboratory of the University of Lund) was installed.

Temperature calibration and stability, calorimetric noise level, time constant, calorimetric signal linearity and temperature dependence of the calorimetric sensitivity were evaluated. The changes allowed the achievement of a temperature stability better than ± 0.5 mK, a calorimetric signal noise level around ± 50 nV and a calorimetric sensitivity ranging from 100 (at T = 283 K) to 110 mV/W (at T = 333 K).

For the high precision heat capacity measurements, the incremental temperature step method was implemented. Sapphire (NBS SRM 720) was used as calibrant and the overall performance of the system was tested with recommended substances, namely benzoic acid, anthracene and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ($[C_6C_1im][NTf_2]$). The obtained results revealed low dispersion (0.5 %) and an uncertainty better than 1 % (for a temperature range from 283 to 333 K).

The new *i*Sense*DSC* microcalorimeter system (refurbished and upgraded version of the SETARAM microDSC III) was able to reproduce data reported in the literature, which was obtained with high-precision techniques (namely adiabatic calorimetry and drop microcalorimetry).

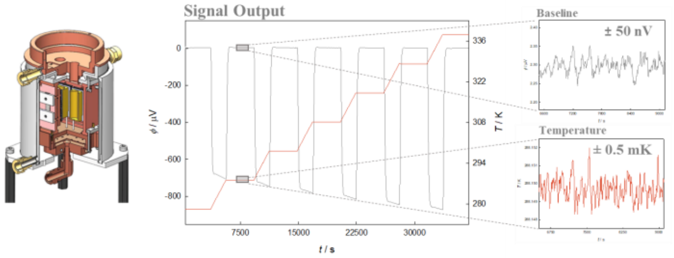

Fig.1. Representation of the calorimetric block and detail of the signal and temperature readings.

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Exploring the effect of nanostructuration on the thermophysical properties of the 1-alkyl-3-methylimidazolium triflate series

Ana I. M. C. Lobo Ferreira[*], **Rodrigo M. A. Silva, Luís M. N. B. F. Santos**

CIQUP, Institute of Molecular Sciences (IMS) – Department of Chemistry and Biochemistry, Faculty of Sciences,
University of Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
**ana.ferreira@fc.up.pt*

Nowadays it is widely accepted that, in the liquid phase, ionic liquids exist as nanostructured fluids. When the alkyl side chains of the cations are long enough, they tend to segregate, giving rise to two distinct nanodomains: a polar nanodomain (where the cationic head groups and the anions are located) and a non-polar domain (where the end parts of the alkyl tails are located) [1]. In this work, we studied the phase behavior, heat capacity and volatility of the 1-alkyl-3-methylimidazolium triflate series, $[C_nC_1im][OTf]$ (with $n = 2, 4, 6, 8, 10, 12$).

The phase behavior was studied by differential scanning calorimetry (DSC). The heat capacity of this IL series was determined, as a function of temperature (between 283 K and 333 K), using a customized differential scanning microcalorimeter (*iSenseDSC*) and, at $T = 298.15$ K, using a drop microcalorimeter [2]. The volatility was measured by means of a Knudsen effusion method coupled with a quartz crystal microbalance (KNQ) [3].

The trend of the specific, volumetric heat capacities and volatility along the number of carbon atoms in the alkyl chain, n, highlights a trend shift at $n = 6$ (critical alkyl size, CAS). The volumetric heat capacity reaches a minimum at $n = 6$, evidencing the intensification of the nanostructuration [4,5].

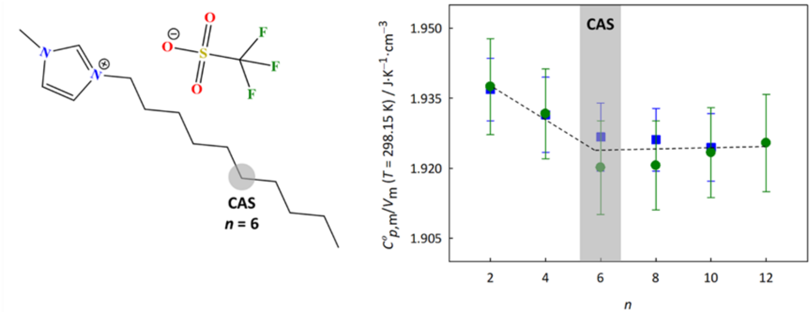

Fig.1. Molecular structure of the $[C_nC_1im][OTf]$ ionic liquid, and volumetric heat capacity ($C^{\circ}_{p,m}/V_m$), at $T = 298.15$ K, as a function of the number of carbon atoms (n) in the alkyl side chain of the cation. ●:*iSenseDSC*, ■: drop calorimetry. "CAS" means "critical alkyl size".

Acknowlegdements
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

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Extensive Study of the Electrical Conductivity of Imidazolium Ionic Liquids: the Anion Effect

Carlos F. P. Miranda*, L. M. N. B. F. Santos

CIQUP, Institute of Molecular Sciences (IMS)- Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua Campo Alegre, 4169-007 Porto, Portugal
**e-mail: carlospesqueiramiranda@gmail.com*.

This work presents an extensive study of the anion effect on the electrical conductivity of ionic liquids. The electrical conductivities of four ILs composed by the 1-butyl-3-methylimidazolium cation $[C_4C_1im]^+$ and bis(trifluoromethylsulfonyl)imide (NTf_2), trifluoromethanesulfonate (OTf), hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-) anions were measured using a multi-frequency impedance methodology. The measurements were conducted between 283 and 333 K and were based on the scanning of resistance, *R*, and reactance, *X*, from 20 Hz to 500 kHz. The electrical conductivity of the ionic liquids was derived from the extrapolation of resistance to infinite frequency. The utilization of this analytical procedure in combination with the multi-frequency scanning allows the mitigation of polarization effects.

The experimental scanning showed that the effect of the anion was not only observed on the magnitude of the electrical conductivity but also on the shape of the R and X spectrums.

The Vogel-Fulcher-Tammann (VTF) equation was used to fit the conductivity – temperature data, $\sigma(T)$ as well as to derive the pre-exponential coefficient and energy of barrier. From the data the follow trend of electrical conductivity was found, $NTf_2 \sim BF_4^- > OTf > PF_6^-$ (Figure 1). The results show that the electrical conductivity is dependent of anion shape and interaction potential between the ions, which are well described by the pre-exponential coefficient and energy of barrier, respectively. Additionally, it was found that conductivity-temperature dependence could be strong enough to change the order of conductivity in the ILs.

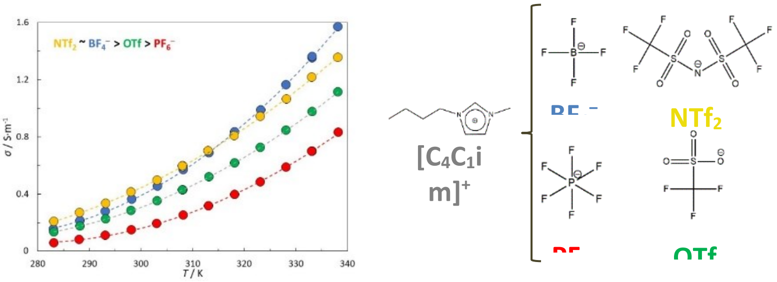

Fig.1. Electrical conductivity as a function of temperature for the studied imidazolium ionic liquids.

Acknowledgements

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Energetic study of methyl-indanones with potential application in thermochemical processes

Ana L.R. Silva[*], **Maria D.M.C. Ribeiro da Silva**

Centro de Investigação em Química (CIQUP) - Instituto de Ciências
Moleculares (IMS), Department of Chemistry and Biochemistry, Faculty of
Sciences, University of Porto, Rua do Campo Alegre, P-4169-007 Porto,
Portugal
**analuisa.rs@fc.up.pt*

Accurate data of thermochemical and thermophysical properties of key organic compounds are very relevant when controlling experimental investigations to produce value-added chemical products, as those related with biomass. This information can be also used in the development of schemes for the prediction of the homologous properties of related compounds, in particular, modeling studies for the prediction of bio-oil composition. In this context, our research group has been involved in an extensive experimental and theoretical thermodynamic study on key biomass-derived compounds, namely, vanillyl alcohol [1], levoglucosan [2], cellulose allomorphs [3], and more recently, cyclopentenones [4], and indanones [5].

This work reports an experimental and computational study of thermodynamic properties of two methyl-1-indanones. The parameters determined and presented for each indanone are the standard enthalpy of formation of the compound, both in the solid and gaseous phases, at T = 298.15 K, and the respective enthalpy of vaporization. The experimental techniques used are mainly calorimetric, being also performed high level ab initio calculations to obtain the gas-phase standard molar enthalpy of formation of both indanones. Some energetic and structural correlations will be analysed by comparison of the results herein with other compounds structurally related.

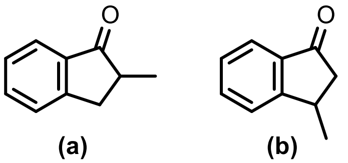

Fig.1. Methyl-indanones studied: 2-methyl-1-indanone (a) and 3-methyl-1-indanone (b).

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Uso do intercalador Laranxa de tiazol para a detección e cuantificación de ADN de dobre febra

Stella Hernández[1]*, Lucas Piñeiro[1], Mercedes Novo[1], Wajih Al-Soufi[1]

[1] Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela, E-27002 Lugo, España
* *stella.hernandez@rai.usc.es*

O Laranxa de tiazol (TO) é un colorante intercalador de ADN con potencial aplicación para a detección de dobres cadeas de ADN (dsDNA) e para a súa cuantificación durante a amplificación mediante a reacción en cadea da polimerasa (PCR). Isto debese a que o TO practicamente non emite fluorescencia cando está en disolución acuosa pero emite case 20000 veces máis cando esta unido ao dsDNA [1]. Na bibliografía descríbense altas constantes de afinidade para a complexación do TO co dsDNA, así como estudos da selectividade do TO para avaliar seu potencial como intercalador [2,3]. Tamén se estudaron as interaccións do TO con outras conformacións do ADN como os G-cuadruplexos [4].

A intercalación ocorre cando o ligando ten un tamaño óptimo e unha natureza química para que permita o intercalador encaixar entre os pares de base do ADN. Aínda así, a afinidade entre o intercalador (TO no noso caso) e a dsDNA pode variar debido ás condicións experimentais, especialmente a carga e a concentración do catión presente na solución.

Neste traballo realizamos medidas de espectroscopia de fluorescencia de estado estacionario e de tempos de vida de fluorescencia para estudar a interacción entre o TO e o dsDNA e analizar os efectos da concentración e carga do catión na constante de unión usando NaCl e $MgCl_2$. Tamén se estudou o posible efecto do tamaño das cadeas de dsDNA na constante de afinidade, usando cadeas cortas tipo *hairpin* ou cadeas largas como o Lambda-DNA.

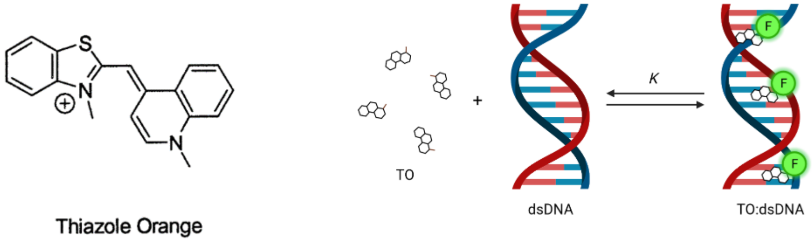

Fig.1. Esquerda: Estrutura molecular do TO. Dereita: Esquema da interacción entre TO e dsADN.

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QUÍMICA INORGÁNICA

A metal-coordination-triggered carbamate hydrolysis process

M. Martínez-Calvo[1,*], **S. Fernández Fariña**[1], **Á. Sánchez-González**[1],
M. Maneiro[2], **A. M. González-Noya**[1]

[1]Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Terra, 27002, Lugo, Spain]
**miguel.martinez.calvo@usc.es*

Carbamates are compounds of great interest due to their potential applications in different fields such as new materials [1] or nanomedicine [2]. To date, it should be highlighted that some examples of platinum(IV) carbamate derivatives have been described as prodrugs with the aim of minimise side effects of platinum(II) drugs used to treat cancer disease [3].

In view of these studies, in this communication we were focused on the conditions under which carbamate ligands can be hydrolyzed. We have analysed the coordination behaviour of a carbamate ligand in its neutral form with different metal chloride salts. Interestingly, we have observed a hydrolysis process of the carbamate ligand, releasing dihydrazone mononuclear complexes, carbon dioxide and a alcohol species corresponding to the pendant groups of the carbamate (Figure 1). A plausible mechanism for this process has been proposed, which has been supported by ^{1}HNMR and MS spectroscopy studies as well as by X-ray diffraction studies.

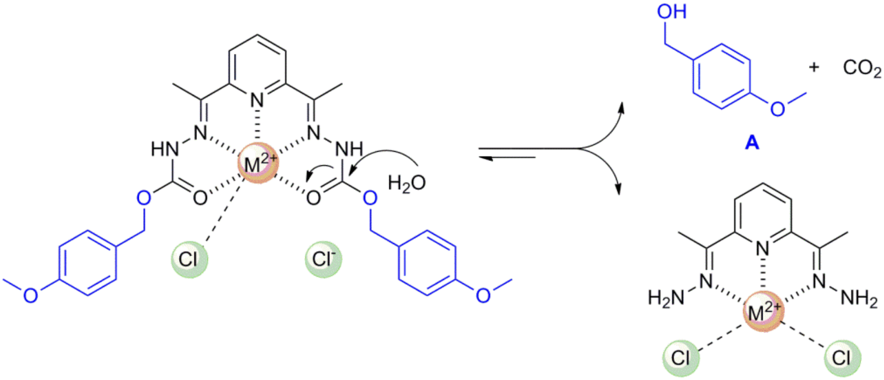

Figure 1. Hydrolysis process of the carbamate ligand.

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A magneto-structural study of a mononuclear dysprosium complex with a Schiff base *N*₆ donor

Cristina González-Barreira[1,*], Julio Corredoira-Vázquez[1,2], Ana M. García-Deibe[1], Jesús Sanmartín-Matalobos[1,3], Matilde Fondo[1]

[1] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2] Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal
[3] Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
cristina.gonzalez.barreira@rai.usc.es

Lanthanoid molecule magnets occupy a preferential place in the field of molecular magnetism.[1] Among them, dysprosium complexes with an axial geometry have so far generated the best results,[2] reaching the highest blocking temperatures (T_B), the record being at 80 K.[3,4] But these molecule magnets with high T_B are unstable in air. For this reason, the design of stable, highly axial dysprosium metal complexes capable of generating high magnetic anisotropy remains a challenge. One of the various alternatives that have been considered for this purpose is to obtain pentagonal or hexagonal bipyramidal complexes with N-donor ligands in the equatorial plane, and anionic O-donor ligands in the apical positions.[6]

With these considerations in mind, we present herein the synthesis, structural and magnetic characterization of the mononuclear complex $[DyL^{N6}(OAc)_2](NO_3)\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$), shown in Figure 1.

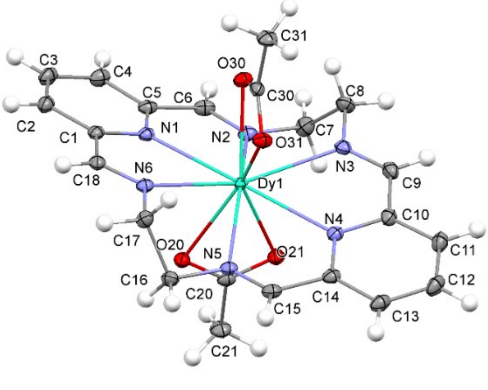

Fig.1. Ellipsoids diagram (50% probability) for the $[DyL^{N6}(OAc)_2]^+$ cation in $\mathbf{1}\cdot 2H_2O$

Acknowledgments

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Luminescent cyclometalated Pt^{IV} compounds bearing phenanthroline-based ligands with antiproliferative activity

Andrea Corral[1], **David Gómez de Segura**[1], **Elena Lalinde**[1], **Mª Teresa Moreno**[1], **Icíar P. López**[2], **José G. Pichel**[2]

[1] Departamento de Química-Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Madre de Dios 53, E-26006, Logroño, Spain

[2] Lung Cancer and Respiratory Diseases Unit (CIBIR). Fundación Rioja Salud. 26006 Logroño (Spain)

**ancorrz@unirioja.es*

Cyclometalated Pt^{II} complexes have been extensively studied due to their interesting optical properties with potential application in light-based technologies and processes [1]. Furthermore, some luminescent cyclometalated Pt^{II} exhibit anticancer activity, which make them potential luminescent probes for DNA and allows easy tracing of their cellular uptake and distribution by confocal microscopy. Much less attention has been devoted to cyclometalated Pt^{IV} compounds, both in luminescence and in biological activity, in spite of their promising properties.

Following with our interest in the study of luminescent cyclometalated Pt^{IV} complexes [2], and considering that the 2-arylbenzothiazole chromophores have been employed to obtain emissive Pt^{II} complexes with promising antiproliferative activity [3], in this work we present a series of dicationic bis-cyclometalated Pt^{IV} compounds based on 2-phenylbenzothiazole (pbt) and phenanthroline-based ligands of the type $[Pt(pbt)_2(N^\wedge N)](ClO_4)_2$ ($N^\wedge N$ = phen **3**; pyraphen **4**; NH_2-phen **5**), using $[Pt(pbt)_2Cl_2]$ (**2**) as precursor. The complexes have been fully characterized and their luminescent properties evaluated in several media (CH_3CN solution, solid state, 298 and 77 K and PS film), supported by theoretical calculations. Additionally, we present a study of their antiproliferative activity towards the A549 cell line (lung cancer) along with their lipophilicity behavior.

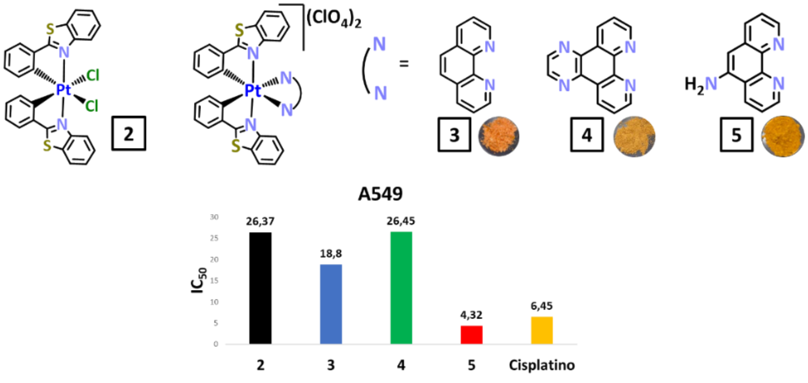

Figura 4. Compuestos sintetizados y resultados en línea tumoral de pulmón A549

Acknowledgments

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QI12

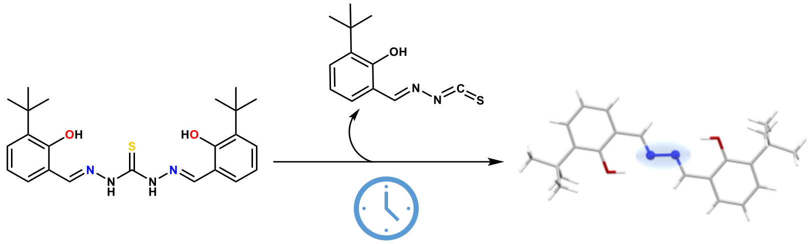
Obtaining an azine ligand via a thiocarbohydrazone desulfurization process

U. Barreiro-Sisto[1,*], **S. Fernández-Fariña**[1], **I. Velo-Heleno**[1], **M. Martínez-Calvo**[1], **R. Pedrido**[1]

[1]Departamento de Química Inorgánica, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
**uxia.barreiro.sisto@rai.usc.es*

A desulfurization process consists on an oxidation reaction in which an elimination of a sulfur atom takes place leading to the formation of a new product. This process has been studied in the case of some thiosemicarbazone ligands and their derivative complexes [1]. However, to date, only one example of a thiocarbohydrazone desulfurization has been found in the literature [2].

In this communication, we were focused on the study of the influence of the reaction time on the isolation of the azine ligand H_2L^1 by means of a desulfurization process of a thiocarbohydrazone ligand H_2L (Figure 1). Different characterization techniques such as X-ray diffraction, ^1H NMR and mass spectroscopy together with literature reports [3], allow us to propose a plausible mechanism to explain the formation of the azine product through a desulfurization process of the thiocarbohydrazone H_2L.



H_2L H_2L^1

Figure1. Obtainment of an azine ligand via thiocarbohydrazone desulfurization process.

Acknowledgements

The research leading to these results has received funding from the following FEDER cofounded-grants. From Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia, 2017GRCGI-1682 (ED431C2017/01), 2018GRCGI-1584 (ED431C2018/13), MetalBIONetwork (ED431D2017/01). From Ministerio de Ciencia, Innovación y Universidades, METALBIO (CTQ2017-90802-REDT). From Ministerio de Ciencia e Innovación (MCIN), MultiMetDRUGS (RED2018-102471-T) and Project PID2021-127531NB-I00 (AEI/10.13039/501100011033/FEDER, UE).

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Inorganic nanoparticles for the detection of circulating proteins associated with the response/resistance to neoadjuvant chemotherapy in HER2-positive breast cancer

<u>Cristina Núñez</u>[1,*], Susana B. Bravo López[2], María del Pilar Chantada-Vázquez[2]

[1]Inorganic Chemistry Department, Universidade de Santiago de Compostela, Facultade de Ciencias, 27002 Lugo, Spain
[2]Proteomic Unit, Health Research Institute of Santiago de Compostela (IDIS), University Clinical Hospital of Santiago de Compostela (CHUS), 15706 Santiago de Compostela, Spain
**cristina.nunez.gonzalez@usc.es*

The unique features of gold (AuNPs) [1] and platinum nanoparticles (PtNPs) [2] make them suitable sorbent nanomaterials with important biomedical applications. In the present study, the interaction of AuNPs (10.02 ± 0.91 nm) and PtNPs (2.40 ± 0.30 nm) with the sera of HER2-positive breast cancer (BC) patients obtained before neoadjuvant chemotherapy (NAC) allowed the pre-concentration of the low-abundance proteins through the protein corona (PC) formation. Then, an exhaustive large-scale LC-MS/MS-based qualitative and quantitative proteomic analysis of the PCs and the crude sera samples (without NPs) was carried out to explore potential circulating protein biomarkers useful to predict the therapeutic response of HER2-positive BC patients treated with NAC (Figure 1).

The results of this study suggest that the identification of some complement and coagulation related circulating proteins constitute a signature that is significantly related to the NAC effect in HER2+ BC patients. Importantly, this novel methodology represents a useful tool to support clinical decision-making in HER2-positive BC patients.

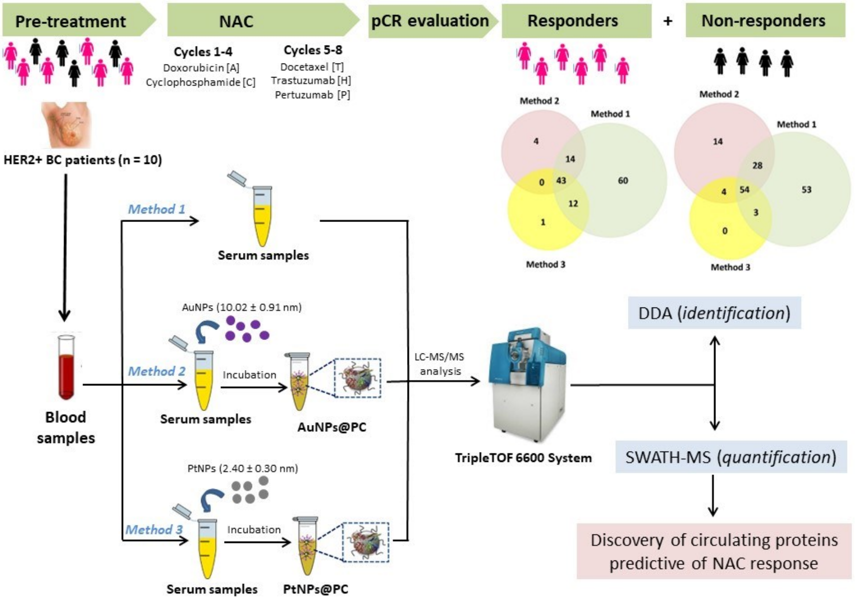

Fig.1. A schematic representation of the experimental workflow.

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QI14

Silver nanoparticles for the detection of circulating serum protein biomarkers of non-muscle invasive bladder cancer

María del Pilar Chantada-Vázquez[1,*], Susana B. Bravo López[1], Cristina Núñez[2]

[1]Proteomic Unit, Health Research Institute of Santiago de Compostela (IDIS), University Clinical Hospital of Santiago de Compostela (CHUS), 15706 Santiago de Compostela, Spain
[2]Inorganic Chemistry Department, Universidade de Santiago de Compostela, Facultade de Ciencias, 27002 Lugo, Spain
**mariadelpilarchantadavazquez@gmail.com*

Bladder cancer (BC) is the second most common cancer of the genitourinary tract and one of the leading causes of death worldwide [1]. BC manifests as either muscle-invasive (MIBC) or non-muscle-invasive (NMIBC), the latter being the predominant form, comprising about 80% of cases [2]. Because 10-year recurrence rates of NMIBC are as high as 74.3%, cystoscopy is recommended routinely for surveillance, which contributes to increased expense and a higher risk for other urologic diseases in the patient [3,4].

Because cystoscopy is expensive and invasive, a new method of detecting NMIBC is needed. This study aims to identify potential serum protein markers for NMIBC to improve diagnosis and to find treatment approaches that avoid disease progression to a life-threatening phenotype (MIBC). Here, silver nanoparticles (AgNPs, 9.73 ± 1.70 nm) as a scavenging device together with sequential window acquisition of all theoretical mass spectra (SWATH-MS) were used to quantitatively analyze the blood serum protein alterations in two NMIBC subtypes, T1 and Ta, and they were compared to normal samples (HC) (Figure 1). NMIBC's analysis of serum samples identified three major groups of proteins, the relative content of which is different from the HC content: proteins implicated in the complement and coagulation cascade pathways and apolipoproteins. In conclusion, many biomarker proteins were identified that merit further examination to validate their useful significance and utility within the clinical management of NMIBC patients.

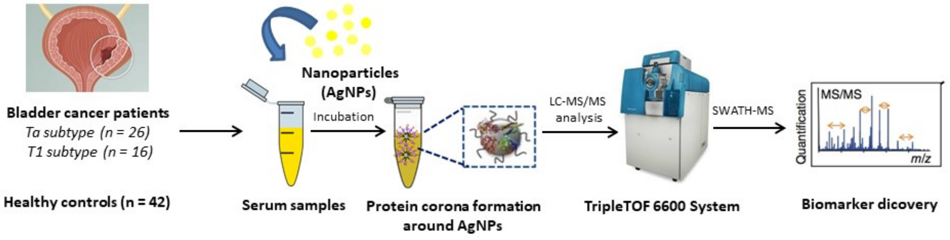

Fig.1. Schematic representation of the methodology developed for the PC formation around AgNPs (9.73 ± 1.70 nm) after the *ex vivo* incubation with samples from healthy controls (HC) (n = 42) and NMIBC patients (n = 42). The quantitative analysis of the PCs was developed by SWATH-MS for the detection of circulating protein biomarkers.

Acknowledgments
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Síntese de hidrocarburos iridaaromáticos policíclicos

I. Vázquez-Carballo, M. Talavera, S. Bolaño

Departamento de Química Inorgánica, Facultade de Química, Edificio de Ciencias Experimentais,
Universidade de Vigo, 36310 Vigo, España
**irenvazquez@alumnos.uvigo.gal*

Tomando coma modelo a estrutura do grafeno dopado, e co obxectivo de acadar unha mellora das súas propiedades, actualmente existe un gran interese na obtención e estudo de sistemas análogos a fragmentos de grafeno ou nanografenos baseados na substitución dun átomo de carbono por un metal de transición coma o iridio [1].

Así, este traballo centrouse na síntese de hidrocarburos iridaaromáticos policíclicos (PIrAHs) como primeira aproximación ao obxectivo proposto. Para isto, levouse a cabo un estudo da reactividade dos alcois proparxílicos **I**, **II** e **III** (Figura 1) co complexo $[IrCp^*Cl(NCMe)(PMe_3)]PF_6$. Co alcol proparxílico **I** obtívose o produto buscado *(±)(S,P)/(S,M)*-$[IrCp^*(PMe_3)(\kappa^2C^1,C^{9a}\text{-}L^1)]PF_6$ (L^1={=C(OMe)–CH=C(1-$C_{10}H_6$)(1-$C_{10}H_7$)}) [2]; co **II** non foi posíbel acadar a formación do PIrAH; e co **III** si puido confirmarse a obtención de $[Ir_2Cp^*_2(PMe_3)_2(\mu\text{-}1\kappa^2C^1,C^{\alpha}:2\kappa^2C^{1'}C^{\alpha'}\text{-}L^2)](PF_6)_2$ (L^2={=C(OMe)-CH=C{(C_6H_3)(C_6H_4)}C=C {(C_6H_3)(C_6H_4)}C=CH-C(OMe)=}) aínda que aparece coma mestura de diferentes isómeros (Figura 1).

Mediante as técnicas de resonancia magnética nuclear (RMN) e espectrometría de masas de ionización por electrospray (MS-ESI) foi posíbel a identificación e caracterización dos diferentes produtos.

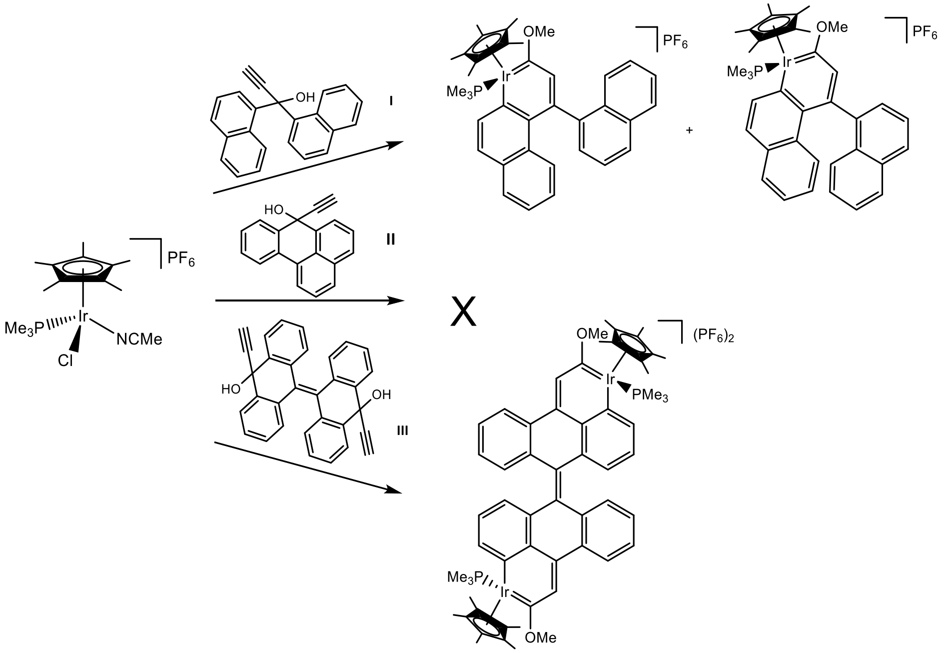

Fig.1. Esquema xeral do traballo realizado.

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QI16

A new peroxo-complex of dysprosium with single-molecule magnet behaviour

Julio Corredoira-Vázquez[1,2*], Paula Oreiro-Martinez[2], Ana M. García-Deibe[2], Jesús Sanmartín-Matalobos[2,3], Matilde Fondo[2]

[1]Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal
[2]Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[3] Institute of Materials (iMATUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
**julio.corredoira.vazquez@usc.es*

Since the publication of the first single molecule magnet (SMM) in 1993 [1], the search for new molecule-based materials has been a very active area of research [2]. A turning point in this field was marked by the shift from transition metals to lanthanoids (Ln), which inherently show a high ground state spin and large magnetic anisotropy.

Additionally, although Ln^{III} ions are hard acids, very few compounds with this type of metal and the hard base peroxo have been described [3]. The source of these peroxo ions is in some cases uncertain, as they do not always come from the fixation of atmospheric oxygen. In addition, some of these peroxo complexes exhibit single molecule magnet behaviour [3],[4].

By mixing the two fields, that of peroxo-complexes and that of lanthanoid SMMs, we present herein the synthesis, structural and magnetic characterisation of $[Dy_5(H_2L)_2(H_{2.5}L)_2(NO_3)_4(\mu_3\text{-}O_2)_2]\cdot 2H_2O$ (**1**), obtained from the flexible aminophenol ligand H_4L^r (Figure 1).

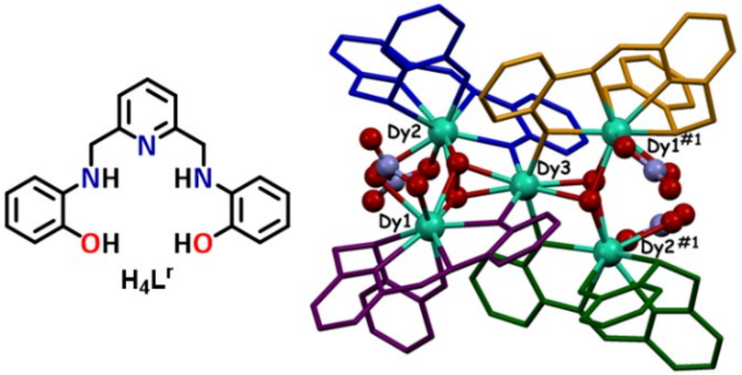

Fig.1. Scheme of aminophenol ligand H_4L^r (left), and crystal structure of the peroxo-complex **1** (right)

Acknowledgements
Authors thank the Spanish Ministerio de Innovación, Ciencia y Universidades (PGC2018 102052-B-C21), and Xunta de Galicia for financial support. J.C.V also thanks Xunta de Galicia for his postdoctoral fellowship (ED481B-2022-068).

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Synthesis of tridentate [*C, N, S*] iminophosphorane cyclometallated palladium compounds

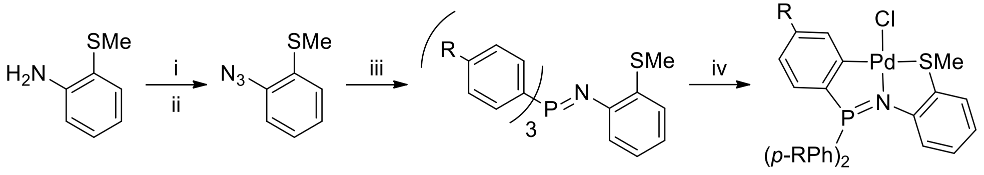
Marcos Rúa-Sueiro, Francisco Reigosa, José M. Vila

Department of Inorganic Chemistry, Faculty of Chemistry, Avda. das Ciencias s/n,
University of Santiago de Compostela
marcos.rua.sueiro@usc.es

The chemistry of cyclometallated compounds, in particular those with palladium, has been of great relevance since their beginning due to their applications in cross-coupling reactions with C-C bond formation (Suzuki-Miyaura[1] or Mizoroki-Heck[2]) and C-N bond formation (Buchwald-Hartwig[3]). Also, they present activity as antitumor or anticancer agents, in some cases similarly to *cis*-platinum.[4]

Iminophosphoranes are ligands characterized by having a P=N double bond, analogous to the phosphorus ylides. The polarization of the P=N double bond allows the nitrogen atom to easily bind to a metal center. This ability has been widely used in coordination and organometallic chemistry.[5,6]

Here in, the synthesis of iminophosphorane palladacycles derived from 2-methylthioaniline is discussed. The 2-methylthiophenyl azide was readily synthesized after *in situ* formation of the diazonium salt. Then, azide 1 was reacted with two different phosphines, following the Staudinger reaction, to give the corresponding iminophosphorane ligands, which yielded complexes with the ligand coordinated to palladium through the *ortho* aromatic carbon, the nitrogen and the sulfur atoms.
Characterization was carried out using Elemental Analysis (C, H, N, S), IR spectroscopy, ^{1}H NMR and $^{31}P\text{-}\{^{1}H\}$ NMR spectroscopies.



1

R = OMe 2a
R = Me 2b

R = OMe 3a
R = Me 3b

i) $NaNO_2$, AcOEt/H_2O; ii) NaN_3, AcOEt/H_2O; iii) 1:1 P(*p*-RPh)$_3$, ether; iv) Na_2PdCl_4, NaOAc, MeOH.

Acknowledgements

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Active antitumoral thiosemicarbazone platinacycles

F. Reigosa[1,*], M. Rúa-Sueiro[1], J.M. Vila[1]

[1]Departamento de Química Inorgánica, Universidad de Santiago de Compostela, av. de las Ciencias, s/n, Santiago de Compostela, Spain
*francisco.reigosa@usc.es

Cyclometallated compounds have been known for decades, but their properties and applicability in different fields has kept researchers to still be interested in their study. Palladacycles have been researched and applied as catalysts in many types of reactions due to their activity and stability, as well as the possibility of obtaining water-soluble compounds[1,2]. Another important field of interest related to cyclometallated compounds is the biomedical one, where metallacycles containing more than one metal center have been studied in treatment of diseases such as malaria,[3] and in cancer. As for the antitumoral aspect, their target is to improve the effect of reference-drugs such as cis-platin, to diminish the side effects and to improve the overall well-being of the patients[4,5].

In this work, a series of boronic acid-bearing thiosemicarbazone platinacycles has been synthesized and characterized by IR, ^{1}H and ^{31}P NMR and, when suitable crystals were obtained, X-ray diffraction. Then, the effect of the substituents and ancillary ligands on the antitumoral effect of the platinacycles was studied in proliferation assays.

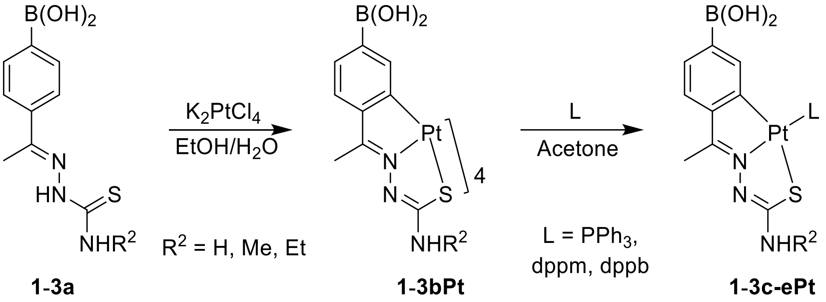

Fig.1. Synthetic Scheme

Acknowledgements
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QUÍMICA ORGÁNICA

QO25

Larvicidal activity of the fungus *Penicillium sp.* 27 against *Culex quinquefasciatus*

Antonio Fernando Vasconcelos Cavalcante Braga[1]*, Antônio José Cantanhede Filho[1], Cristina de Andrade Monteiro[1], Clenilma Marques Brandão[1]

[1]Postgraduate Program in Chemistry (PPGQ/IFMA), Federal Institute of Education, Science and Technology of Maranhão – IFMA, Campus São Luís Monte Castelo. Av. Getúlio Vargas, nº 04, Monte Castelo, São Luís, Brazil
**vasconcelosfernando@acad.ifma.edu.br*

Mangroves represent a highly productive ecosystem, currently occupying a range of about 181,000 km² on the planet. Where Brazil holds about 7% of the total existing area, comprising approximately 12,250 km² of extension. Fungi are important microorganisms for the maintenance of this ecosystem. In addition, they are sources of secondary metabolites of biotechnological interest. Since the unique characteristics of mangroves collaborate for the development of species with potential biotechnological applications [1].

Regarding pest control, fungal metabolites are considered interesting alternatives concerning biological resistance and environmental pollution [2]. Mosquitoes are a major cause of health problems in many countries. Since they are vectors of various diseases. *Lymphatic filariasis*, also known as elephantiasis, is a tropical disease transmitted by the *Culex quinquefasciatus* (Say) mosquito belonging to the *Culicidae* family. Although the disease is rarely fatal, it affects more than 90 million people around the world causing considerable damage, in addition, the lack of effective treatments for the disease suggests that vector control strategies should be considered [3].

In this sense, the present paper focused on the evaluation of the larvicidal activity of the crude methanolic extract produced from the biomass of the fungus *Penicillium sp.*, strain coded as 27, isolated from the soil of mangrove areas of the island of São Luís, Maranhão – Brazil against larvae of the mosquito of the species *Culex quinquefasciatus* (Say) in its 3rd larval stage. Preliminary evaluations were performed in triplicate with concentrations varying between 100 and 400 µg.mL^{-1} for 48 hours, fig. 1, under laboratory conditions. The assays showed LC$_{50}$ equal to 12.2 µg.mL^{-1}. Demonstrating for the first time the larvicidal and biotechnological potential of the fungus *Penicillium sp.* isolated from this source, an area little studied so far. Furthermore, the preliminary study showed that the metabolites present in the crude extract can serve as environmentally friendly alternatives to commonly used insecticides. Further fractionation studies are still needed in order to verify which specific molecule(s) present in the crude extract present such biological activity.

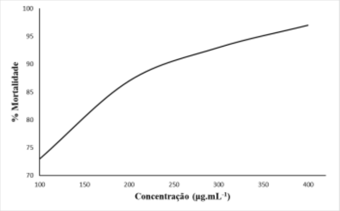

Fig.1. Larval susceptibility of *Culex quinquefasciatus* (Say)

Acknowledgments

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QO26

Photoredox transformations of Quinic Acid

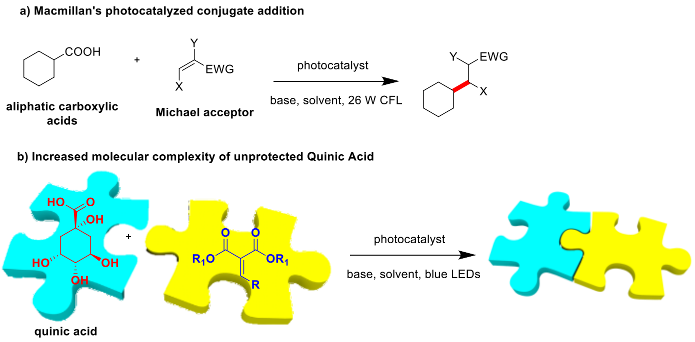
João A. Pacheco[1,*], Nuno R. Candeias[1]

[1]LAQV REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
*joaopacheco@ua.pt

Quinic acid is one of the primary plant metabolites derived from D-glucose and is known to be a valuable chiral building block in the synthesis of natural products.[1] The exploration of quinic acid as a building block for total synthesis or as a synthetic precursor of compounds of relevant biological activity continues to be a topic of research. For instance, while the carbon skeleton of quinic acid was recently deconstructed to build small fragments for synthesis,[2][3] simple transformations such as amidation allowed the preparation of immunosuppressive agents.[4] Notwithstanding the potential of quinic acid as a precursor of interesting useful building blocks, methods for its synthetic manipulation often rely on the use of protecting groups and harsh conditions.

Utilizing the photoredox Michael reaction developed by Macmillan and co-workers[5] that employs carboxylic acids as a traceless activation group, we studied the applicability of this reaction as a novel route of modification of quinic acid. Such protocol was adapted and standardized for a small-scale photoreactor according to the literature.[6] The use of this small setup allowed us to test a series of different conditions and reagents, which proved to be crucial. This strategy allowed increasing the complexity of quinic acid, unravelling a mixture of diastereomers upon formation of an additional ring, as confirmed by ^{1}H NMR techniques.

Our efforts in the optimization of such a method and the structural characterization of the compounds will be presented. While further work is being conducted regarding the scope of the Michael acceptor and catalysts, this reaction has the potential to expand the quinic acid-derived chemical space being envisioned for the creation of new synthetic routes for synthetic chemistry or the preparation of biologically active compounds.


a) Macmillan's photocatalyzed conjugate addition

b) Increased molecular complexity of unprotected Quinic Acid

Fig.1. Macmillan's previous work on decarboxylative Michael addition (a). This work (b).

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Synthesis and structure elucidation of metabolites of the synthetic cathinones pentedrone and methylone for further metabolism studies

Ana Sofia Almeida[1,2,3,4*], **Bárbara Silva**[3,4], **Fernando Remião**[3,4], **Carla Fernandes**[1,2]

[1] Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto
[2] Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto
[3] UCIBIO – Applied Molecular Biosciences Unit, REQUIMTE, laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto
[4] Associate Laboratory i4HB - Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto
**Email: anasofiaalmeida1998@gmail.com*

New psychoactive substances (NPS) represent a public health threat since they are sold as legal alternatives to illicit drugs, are easily accessible online and there is limited information about their properties [1]. Among them, synthetic cathinones are widely abused due to their psychostimulant effects being pentedrone and methylone one of the most consumed NPS in the USA and Europe [2]. Thus, studying their toxicokinetic and toxicodynamic properties is of great importance.

Drug metabolism studies provide key information to allow a better understanding of the pharmacological and toxicological action of drugs [3]. *In vivo* and *in vitro* studies have showed that methylone can undergo *N*-demethylation, *O*-demethylation, *N*-oxidation, and β-keto reduction [4]. For pentedrone, metabolites resulting from *N*-demethylation and β-keto reduction followed by *N*-demethylation have been described [5].

In this work, the synthesis of dihydropentedrone and dihydromethylone, two metabolites of the synthetic cathinones pentedrone and methylone, was performed by keto group reduction of the respective cathinone using sodium borohydride. The synthetic strategy used offered good yields (64–96%). Further structure elucidation was established by spectroscopic methods (IR, GC-MS, ^{1}H and ^{13}C NMR).

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QO28

Discovery of new eugenol-azole hybrids as candidates of potent trypanocidal agents

José Vaz Cardoso Machado[1], Sarah Ferreira Maciel[1], Thayane Silva de Carvalho[3], Viviana Aparecida da Silva[2], Gabriela Francine Martins Lopes[3], Karen Sartori Jeunon Gontijo[3], Valquíria Ângelis Fernandes[2], Jaqueline Maria Siqueira Vieira[3], Lucas Lopardi Franco[1], Lívia de Figueiredo Diniz[2], Diogo Teixeira Carvalho[1]

[1]Federal University of Alfenas, Food and Drug Department Alfenas, Brazil;
[2]Federal University of Alfenas, Department of Patology and Parasitology, Alfenas, Brazil;
[3]Federal University of São João del-Rei, Divinópolis, Brazil.
*jose.machado@sou.unifal-mg.edu.br

Eighteen molecular hybrids based on the fusion of pharmacophore subunities of azole drug and eugenol were designed as potential inhibitors of sterol 14α-demethylase, an enzyme involved in ergosterol biosynthesis. That sterol is an essential component of fungal and trypanosomatides cell membranes and molecular target explored in new drug research. These hybrids were synthesized, characterized and their potential cytotoxic effects were evaluated against *Candida* spp., *Trypanosoma cruzi* trypomastigotes and different mammalian cell lines [1,3].

Results have shown these hybrids have low cytotoxic potential against Vero and H9c2 cells at concentrations under 200 µg/mL [2]. However, none of them has shown antifungal activity against *Candida* spp. in concentration range of 256 to 0,5 µg/mL [3].

Interestingly, in spite of eugenol and analogues had no trypanocidal activity, some hybrids inhibited the viability of *T. cruzi* trypomastigotes at 100 µM. These hybrids may function via different mechanisms than azoles and new studies are being performed on this.

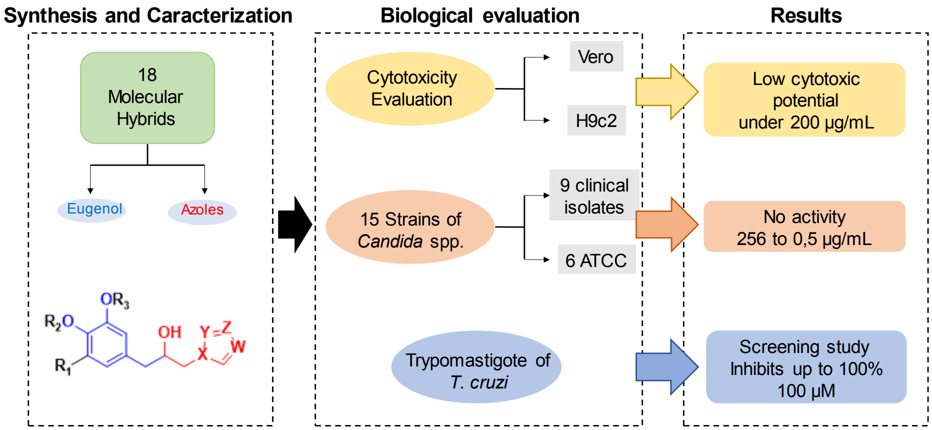

Fig 9: Work summary

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From the bottom of ocean to the lab: synthetic strategies of cyclic peptide marine-derived

Ricardo Ribeiro[1,2*], **Lia Costa**[1], **Eugénia Pinto**[2,3], **Emília Sousa**[1,2], **and Carla Fernandes**[1,2].

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal. [2]CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Matosinhos, Portugal. [3]Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal.
**up200902675@up.pt*

Marine peptides represent one of the most versatile sources of therapeutically effective drug molecules [1]. Long-term evolution of marine organisms advanced in the midst of pathogens, and efficient defense mechanisms were developed for the necessary conditions of their survival [2].

Two antibiotic cyclic depsipeptides, unnarmicins A and C, that differ only in the length of the aliphatic chain, were isolated from the fermentation broth of a marine bacterium, *Photobacteria* sp. strain and showed selective growth inhibition against two strains of *Pseudovibrio* [3] and specifically inhibit some fungal ABC transporters including of *Candida albicans* [4].

Herein, we describe the synthetic strategy and the first achievements regarding the total synthesis of a marine-derived cyclic peptide for antimicrobial activity evaluation. Coupling reactions using reagents such as (1-cyano-2-ethoxy-2-3-oxoethylidenaminooxy)-dimethylaminomorpholinocarbenium hexafluorophosphate (COMU) and protection/deprotection *tert*-butyloxycarbonyl/methyl protecting groups methodologies were performed. The structures of synthetized compounds were established by IR and NMR spectral analysis.

Further studies will include the investigation of the antimicrobial activitiy of the synthetic derivative obtained.

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We thank to FCT - Foundation for Science and Technology through the projects UIDB/04423/2020 and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry - CIIMAR)), and under the projects PTDC/CTA-AMB/0853/2021 and EXPL/CTA-AMB/0810/2021 co-financed by COMPETE 2020, Portugal 2020 and the European Union through the ERDF and by FCT through national funds and structured program of R&D&I ATLANTIDA (NORTE-01-0145-FEDER-000040), supported by NORTE2020, through ERDF, and CHIRALSINTESE_APSFCT_IINFACTS_2021. Ricardo Ribeiro also acknowledgement his PhD, BYTPhD program by CIIMAR, grant provided by FCT UI/BD/150912/2021.

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QO30

Curcumin-based molecular probes for fluorescence imaging of fungi

<u>Samuel Guieu</u>[1,2,*], Joana R. M. Ferreira[1], Mariana Alves[3], Bárbara Sousa[3], Sandra I. Vieira[3], Artur M. S. Silva[1], Ângela Cunha[4], Raquel Nunes da Silva[1,3]

[1]LAQV-REQUI*M*TE, Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal
[2]CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal
[3]iBiMED, Department of Medical Sciences, University of Aveiro, Aveiro, Portugal
[4]CESAM, Department of Biology, University of Aveiro, Aveiro, Portugal
**sguieu@ua.pt*

Fluorescence imaging is a powerfull and widely used method to visualize and study living organisms [1]. However, fungi are notoriously difficult to visualize using fluorescence microscopy, given that their cell wall represents a diffusion barrier, and the synthetic organic dyes available are very limited when compared to molecular probes available for other organisms [2]. To fill this gap, curcumin-based molecular probes were designed based on the rationale that curcumin is fluorescent [3] and has moderate toxicity toward fungi, implying its ability to cross the cell wall to reach targets in the intracellular compartment. A family of borondiketonate complexes was synthesized, based on a curcumin backbone [4], tuning their emission color from blue to red (Fig. 1). These probes did not present noticeable toxicity to filamentous fungus and, when applied to their visualization, readily entered the cells and precisely localized in sub-cellular organelles, allowing their visualization.

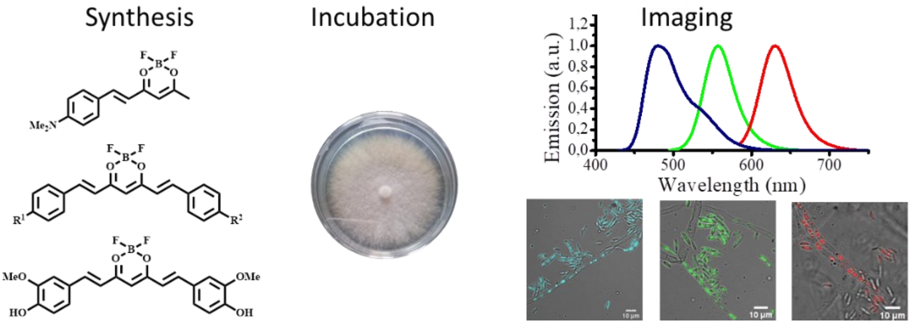

Fig.1. Structures of the synthesized probes (left), photograph of the fungus culture (center), emission spectra and fluorescence miscroscopy of the fungus (right).

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New open-chain carbohydrate amides: synthesis, docking studies and acetylcholinesterase

Ismael M. I.[1,2], Gonçalves-Pereira R.[1,2,3], Figueiredo J.A[1], Lucas S.[4], García-Moreno M.I.[3], Ortiz Mellet C[3], Rauter A. P. [2]

[1]Dep Química, Unidade I&D FibEnTech, Universidade da Beira Interior, Av. Marquês d'Ávila e Bolama, 6201-001 Covilhã, Portugal
[2]Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal
[3]Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, C/Prof. García González 1, 41012 Sevilla, Spain
[4]Department of Medicinal Chemistry, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal
**e-mail del autor de contacto: miismael@fc.ul.pt*

Alzheimer's disease (AD) is the age–related most common cause of dementia among elderly people, and a severe neurodegenerative disorder characterized by progressive memory and cognition losses, leading to disability and inevitably to death [1,2,3,4], considered as an urgent public health problem [5,6,7]. It is the third leading cause of death after cancer and heart diseases [4]. According to an update in 2020 of the estimates given in the World Alzheimer Report 2015 [8,9], there are over 50 million people worldwide living with dementia in 2020. This number will almost double every 20 years, reaching 152 million in 2050. AChE inhibitors are the main stay drugs for early disease stages [2,3].

In this work we report on the development of a synthetic route to yield open chain sugar amides from commercially available carbohydrates. The synthetic pathway starts with diacetone glucose (DAG), which is converted into perbenzyl D-glucono-1,4-lactone in six steps. Reaction with aromatic or aliphatic amines in dichloromethane under reflux (0.5 h to 2 h) afforded the corresponding amides in high yield (80 – 95%) (Scheme 1). Bis(amidation) of a diamine was also accessed by this procedure in 3 h but reaction product was isolated in very low yield (13%). Docking studies and evaluation of acetylcholinesterase inhibition were carried out and the results will be disclosed.

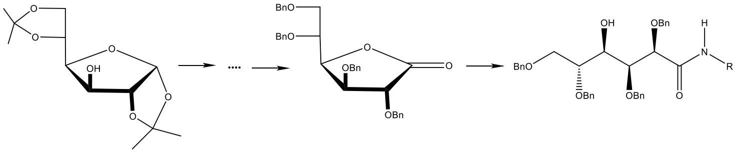

Fig.1. Synthesis of open-chain carbohydrate amides from diacetoneglucose

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QO32

Synthetic access to new fused thiazoloindazole as acetylcholinesterase inhibitors: synthesis, characterization and molecular docking studies

Fatima E. Laghchioua[1,2]*, Carlos F. M. Silva[2], Nuno M. M. Moura [2], Florbela Pereira [3], Diana C. G. A. Pinto[2], M. Amparo F. Faustino[2], J. A. S. Cavaleiro[2], Maria Graça P. M. S. Neves, E. M. Rakib [1,4]

[1] Laboratory of Molecular Chemistry, Materials and Catalysis, Faculty of Sciences and Technics, Sultan Moulay Slimane University, Beni-Mellal, BP 523, Morocco
[2] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[3] LAQV-REQUIMTE, NOVA School of Science and Technology, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[4] Higher School of Technology, Sultan Moulay Slimane University, BP 336, Fkih Ben Salah, Morocco
laghchioua@ua.pt

Acetylcholinesterase (AChE) is the enzyme responsible for the hydrolysis of the neurotransmitter acetylcholine in cholinergic synapses, responsible for mediating the messages between neurons. So, molecules that inhibit or reactivate the AChE enzyme are considered to be potential drugs for Alzheimer's disease or other neurodegenerative diseases, such as amyotrophic lateral sclerosis or Parkinson´s disease [1].

Considering our interest in developing bioactive molecules centred on the indazole unit [2-4], we report here the use of fused thiazoloindazole scaffolds to obtain new compounds with the potential to act as acetylcholinesterase (AChE) inhibitors. The design of the new derivatives based on molecular docking studies, their structural characterization, and preliminary results concerning AChE activity will be presented and discussed.

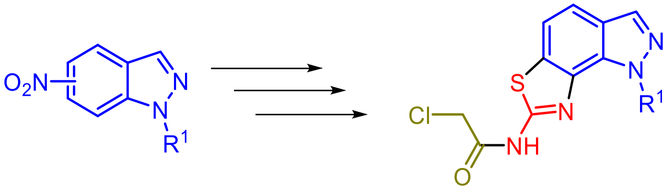

Fig.1. Structure of thiazoloindazole scaffolds obtained from nitroindazoles

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Synthesis of hexahydropyrroquinolines-2,3-diol, analogues of swainsonine, and prediction by molecular modeling of their inhibition power towards human Golgi a-mannosidase II

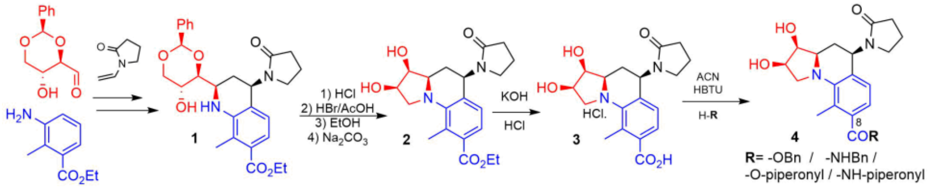
Artem Drogalin [1,*], **Tarsila G. Castro** [2], **Luis S. Monteiro** [1], **Maria J. Alves** [1]

[1]Centro de Química Universidade do Minho. Campus de Gualtar, Escola de Ciências 4710-057 Braga Portugal
[2]Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar
4710-057 Braga, Portugal
**e-mail: id9200@alunos.uminho.pt*

Swainsonine (swa) is a strong inhibitor of mannosidases with a major problem: lack of selectivity between Golgi a-mannosidase II and lysosomal mannosidase. This causes lysosomal storage diseases and prevents swa clinical usefulness [1]. Many efforts have been put around this polyhydroxylated indolizidine molecule, to induce inhibitory selectivity. A major drawback in these studies over the years is the source of the enzyme used to test molecules. In this work were obtained a new type of swa analogues, hexahydropyrroquinolines-2,3-diol (HHPQ), and its inhibitory potencial is estimated by molecular modeling.

The indolizidine nucleus of the target molecules was obtained by a Diels-Alder cycloaddition. It bears a fused aromatic group attached to the 5 and 6 positions, and an ester/amide tail is attached prolonging the structure, compounds **4**. The synthesis starts with the generation of tetrahydroquinoline (THQ) **1** in two steps: 1) condensation of formal D-glyceraldehyde and ethyl 3-amino-2-methylbenzoate, 2) cycloaddition of *N*-vinylpyrrolidone [2]. The THQ structure is transformed into the HHPQ (**2**), in an 84% overall yield. The ester is hydrolyzed to give amino acid **3**, which is coupled with amines/alcohols upon HBTU coupling agent, furnishing final esters/amides (**4**) in 21-79% yields.

To predict the compound´s Golgi mannosidase activity in humans (hGMII) a human enzyme model was generated by homology modeling. The homologous model was relaxed by molecular dynamics at the appropriate pH. The correlation between docking binding energies of bicyclic/monocyclic iminosugars and its enzymatic inhibition (hGMII) values published in the lit. [3] was found. The linear regression obtained will allow to predict K*i* with 80% certainty in a range 10-2200 mM values. The estimated K*i* of the new HHPQ will be presented.



Scheme 1. Synthesis of hexahydropyrroquinolines-2,3-diols

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New 4-aminoacridine-cinnamic acid conjugates as multi-stage antimalarial hits

<u>Mélanie Fonte</u>[1,*], Diana Fontinha[2], Diana Moita[2], Omar Prades[3], Yunuen Padilla[3], Ricardo Ferraz[1,4], Xavier Fernàndez-Busquets[3,5,6], Miguel Prudêncio[2], Paula Gomes[1], Cátia Teixeira[1,7]

[1]LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal;
[2]Instituto de Medicina Molecular, Faculdade de Medicina, Universidade de Lisboa, Portugal;
[3]Nanomalaria Group, Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Spain;
[4]Ciências Químicas e das Biomoléculas, Escola Superior de Saúde, Politécnico do Porto, Portugal;
[5]Barcelona Institute for Global Health (ISGlobal), Barcelona Center for International Health Research (CRESIB), Hospital Clínic-Universitat de Barcelona, Spain;
[6]Nanoscience and Nanotechnology Institute (IN2UB), University of Barcelona, Spain;
[7]current affiliation: Gyros Protein Technologies Inc., Tucson, Arizona, USA
**up201305020@edu.fc.up.pt*

The eradication of malaria remains to be achieved, mainly due to the continued spread of drug-resistant parasites. To overcome this, multi-stage drugs have been prioritized in antimalarial drug discovery, since targeting more than one process in the *Plasmodium*'s life cycle may increase efficiency, while decreasing the chances of resistance emergence by the parasite [1]. Quinacrine (QN) was the first synthetic antiplasmodial drug active against blood forms of the *Plasmodium* parasite but was rapidly superseded by chloroquine (CQ) which has greater safety, efficiency, and bioavailability [2]. Analysing the QN structure, its acridine core is a fusion between the heterocycle core of CQ and primaquine (PQ), another antiplasmodial drug active against liver forms of the parasite, and able to block malaria transmission. A new family of QN derivatives reported by us, 4-aminoacridines, corresponding to the merge of CQ core and PQ, showed moderate dual-stage antimalarial activity [3,4]. We have now developed a second generation of 4-aminoacridines (**Fig.1**) through their conjugation to cinnamic acids (CA) of natural origin that have been reported to enhance antimalarial activity when conjugated to antimalarials [5]. In this communication, we will present the chemical synthesis of this new family of *N*-cinnamoyl-4-aminoacridines and the *in vitro* assessment or their activity against a) liver stages of *P. berghei*, b) erythrocytic forms of *P. falciparum*, and c) early and mature gametocytes of *P. falciparum*. Results demonstrate that the conjugation of the CA moiety to the 4-aminoacridine core delivers new compounds with enhanced *in vitro* activity against all three stages of the malaria parasite lifecycle inside mammalian hosts.

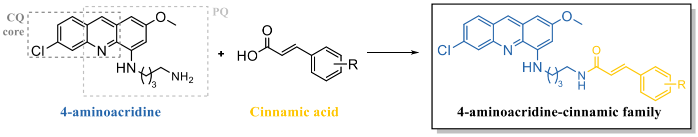

Fig.1. Chemical structure of the N-cinnamoyl-4-aminoacridines family.

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Docking-based Virtual Screening as a tool to identify new small molecules targeting SARS-CoV-2

Francisca Carvalhal[1-4], Andreia Palmeira[1,2], M. Helena Vasconcelos[3-5], Emília Sousa[1,2]
Marta Correia da Silva[1,2*]

[1]Departamento de Ciências Químicas, Laboratório de Química Orgânica e Farmacêutica, Faculdade de Farmácia, Universidade do Porto (FFUP), Porto, Portugal.
[2]CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, Matosinhos, Portugal.
[3]i3S – Instituto de Investigação e Inovação em Saúde, UP, Porto, Portugal.
[4]IPATIMUP – Institute of Molecular Pathology and Immunology of the UP, Porto, Portugal.
[5]Departamento de Ciências Biológicas, Laboratório de Microbiologia, FFUP, Porto, Portugal.
**E-mail: m_correiadasilva@ff.up.pt*; dedicated by the author to the memory of Professor Costa Lima

Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), the causative agent of the COVID-19 disease, has rapidly become a global health pandemic. The variants of SARS-CoV-2 suffered several mutations, some of them specific to the spike protein portion of the virus, responsible for its attachment into host cells [1]. Thus, research on inhibiting viral attachment to the host receptors is still essential. Glucose-Regulated Protein 78 (GRP78) has been described as a critical cofactor for productive infection [2]. Several virtual [3] and *in vitro* studies [2], as well as case studies [4], suggest that inhibiting the interaction between SARS-CoV-2 spike protein and cell surface GRP78 could possibly decrease the rate of viral infection. Design and/or development of small molecules that limit viral infection is crucial [5].

In Laboratório de Química Orgânica e Farmacêutica (LQOF), several small molecules have been obtained in the last decade and promising hits were discovered particularly with antiviral activity [6]. In this work, a docking study was performed with approximately 300 small molecules from LQOF, in the substrate binding domain (SBD) of GRP78 (PDB 5E84). Thirty-one compounds revealed better or equal docking scores than the positive control (region IV from SARS-CoV-2 spike). Following, a hybridization approach was applied generating approximately 100 new molecules. From the designed molecules, 19 presented higher capacity to interact with SBD GRP78 (better docking scores) than the first ones. In thefuture, these molecules will be synthetized and its in silico prediction further accessed by in vitro testing.

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QO36

Preparation benzoporphyrin-based photosensitizers

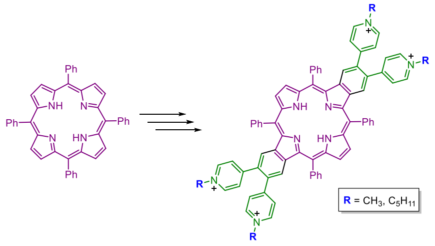
Filipe M. P. Morais[1], Cátia Vieira[2], Ana T. P. C. Gomes[2], Maria A. F. Faustino[1], Adelaide Almeida[2], Maria G. P. M. S Neves[1], Nuno M. M. Moura[1,*]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2] CESAM, Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal
* nmoura@ua.pt

The employment of antimicrobial therapy in clinical practice has been one of the most successful advances in modern medicine and has resulted in an increase in the life expectancy of the world's population. However, the misuse and overuse of antibiotics has caused the development of bacteria resistant strains to antimicrobial agents, which, together with the lack of therapeutic alternatives and fast spread, leds the World Health Organization to identify antibiotic resistance as one of the three main health threats of the 21st century [1].

Antimicrobial photodynamic therapy (aPDT) is considered a promising alternative to antibiotic treatment, particularly in the case of localized infections. aPDT involves the combination of light, dioxygen and a photosensitizer (PS), producing reactive oxygen species (ROS) that lead to cell inactivation [2]. The absence of resistance development by bacteria to this approach is particularly relevant [3]. Porphyrins have aroused particular interest in the scientific community, showing very promising results in several areas, namely in medicine. In this field, these macrocycles have been shown to be particularly efficient as PS in tumor photodynamic therapy (PDT) and in the inactivation of microorganisms (aPDT) [4,5]. However, the potential of cationic benzoporphyrin derivatives as PS in aPDT remains almost unexplored, although benzoporphyrin derivatives are clinically approved for use in PDT, as is the case of verteporfin (Visudyne®) [2].

In this communication, it will be discussed the synthetic approach to attain efficiently tetracationic benzoporphyrins and their ability to photoinactivate a recombinant bioluminescent *Escherichia coli*.



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We thank the University of Aveiro and FCT/MCT for the financial support for REQUIMTE (UIDB/50006/2020, UIDP/50006/2020), CESAM (UIDP/50017/2020+UIDB/50017/2020+LA/P/0094/2020) and the FCT project PORP2PS (EXPL/QUI-QOR/0586/2021), through national founds and were co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. N.M.M. Moura thanks FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória (REF.-048-88-ARH/2018).

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Synthesis of novel *C*-glycosyl flavonoids

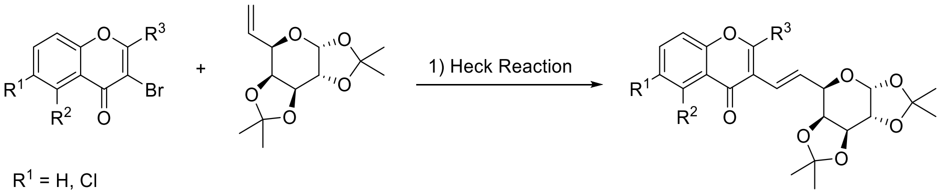
Patrícia Godinho[1,*], **Raquel Soengas[2]**, **Vera L. M. Silva[1]**

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
[2]Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Julián Clavería 7, 33006, Oviedo, Spain
**patricia.godinho@ua.pt*

Flavonoids are a well-known class of oxygenated heterocyclic derivatives, formed as secondary metabolites that are widely distributed in the plant kingdom. Naturally occurring flavonoids are extensively distributed in their glycosidic form, which has an impact on biological properties since it improves the solubility and absorption. In nature, the most common glycosyl flavonoids are the *O*-glycosyl flavonoids; however, *C*-glycosyl flavonoids have attracted recent interest, due to their enhanced stability to chemical and enzymatic hydrolysis. *C*-Glycosyl flavonoids have a wide range of biological activities, including antioxidant, antidiabetic, anticancer, antitumor, antibacterial, and antiviral effects.[1]

There are two main synthetic strategies for the preparation of *C*-glycosyl flavonoids, those based on the *C*-glycosylation before the aglycone formation and those relying on the *C*-glycosylation of the already formed aglycone. [2] The second strategy has proven the most effective and one of the most studied protocols for the formation of carbon-carbon bonds between the aglycone and a sugar moiety are the transition metal-catalysed cross-coupling reactions, such as the Heck reaction. [3]

Therefore, we envisioned the synthesis of a novel class of 3-*C*-glycosyl flavonoids based on the Heck reaction of 3-bromoflavonoids and diacetone-5-*C*-vinyl-L-arabinose (Fig. 1). More details concerning this new synthetic methodology will be presented in this communication.



R^1 = H, Cl
R^2 = H, OMe
R^3 = CH_3, 3,4-bis(benzyloxy)phenyl, 3,4-bis(benzyloxy)styryl, 3,4-dimethoxystyryl, 4-methoxystyryl

Fig.1. Synthesis of *C*-glycosyl flavonoids.

Funding

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Acknowledgments

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Metal Ion Sensors Based on Thiazolo[5,4-*d*]thiazoles

<u>Ana F. R. Cerqueira</u>[1,*], Nuno M. M. Moura[1], Maria G. P. M. S. Neves[1], A. Jorge Parola[2], Augusto C. Tomé[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
*anacerqueira@ua.pt

Thiazolo[5,4-*d*]thiazoles (TzTz) are a class of heterocycles that due to their rigid and coplanar structure, extended π-conjugation and high environmental stability are being considered for different applications [1]. In fact, TzTz were already successfully explored as components of solar cells devices, OLEDs, fluorescent metal-organic frameworks and as photocatalysts [2]. Considering the properties of TzTz, the possibility of using them as sensors is also meriting attention, but as far as we know the number of studies is still limited [3-5].

Herein, we report the synthesis and characterization of TzTz bearing 6-methylpyridin-2-yl moieties with an extended π-conjugated system, as well as their sensing ability towards metal ions.

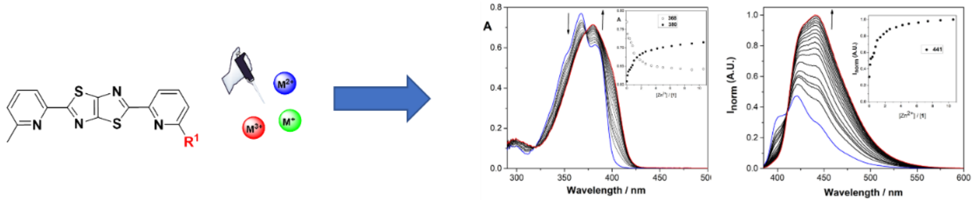

Fig.1.

Acknowledgements: Thanks are due to the University of Aveiro and Fundação para a Ciência e a Tecnologia (FCT) for the financial support to project PTDC/QEQ-QOR/6160/2014 and the LAQV-REQUIMTE (UIDB/50006/2020) through national funds and, where applicable, co-financed by FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. Ana F. R. Cerqueira thanks FCT for her doctoral grant (SFRH/BD/135597/2018). The research contract of N.M.M. Moura (REF.-048-88-ARH/2018) is funded by national funds (OE), through FCT.

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QO39

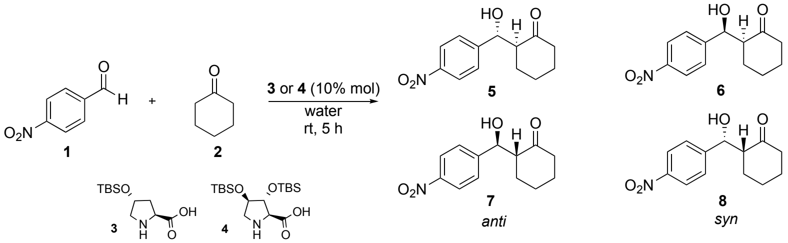
Organocatalytic properties of the iminosugar DAB

<u>Ramón J. Estévez</u>, Rosalino Balo, David Reza, Pablo López and Juan C. Estévez*

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares
and Departamento de Química Orgánica, Campus Vida, Universidade de Santiago de Compostela,
15782 Santiago de Compostela, SPAIN.
*juancarlos.estevez@usc.es

The development of enantioselective reactions using water as a reaction medium and small organic molecules as organocatalysts is an important current goal.[1] Proline is a suitable organocatalyst, because its conformational rigidity, its ability to act as a base and as a Brönsted acid, both allowing it to act as an efficient bifunctional catalyst.[2] Nevertheless, it is not efficient in aqueous media, which require prolines substituted with hydrophobic groups, because most of the reactions take place in the interphase of biphasic systems.[3]. A representative example is the aldol condensation of p-nitrobenzaldehyde with cyclohexanone, using monosubstituted proline **3** as the catalyst and water as the solvent, Four stereoisomers (**5**, **6**, **7** and **8**) resulted, with an overall yield of 86%, an *anti*/*syn* diastereomeric ratio of 20:1 and an enantiomeric excess of greater than 99%.

The organocatalytic properties of proline **4**, with two OH groups protected as OTBS, were now studied for the aldolic condensation of *p*-nitrobenzaldehyde with cyclohexanone, in the same conditions as for proline **3**. The results obtained were almost similar. The enantiomeric yields and the enantiomeric excesses were also 86% and greater than 99%, respectively. But the diastereomeric *anti*/*syn* excess was now higher (25:1 versus 20:1)



Scheme 1

Catalyst	Overall yield	e.e.	*Anti*/*syn* ratio	Major reaction product
3	86%	>99%	20:1	**5**
4	86%	>99%	25:1	**5**

Acknowledgements

This work has received financial support from the European Union (European Regional Development Fund - ERDF), the Xunta de Galicia (Centro Singular de Investigación de Galicia acreditation 2019-2022, ED431G 2019/03; and grants ED431C 2018/30 and ED431C 2018/04).

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Expanding the Library of Cyclopentadienone Iron Tricarbonyl Complexes: Synthesis and Characterization of Novel Precatalysts

M. J. Verganista[1*], N. R. Candeias[1]

[1]LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal;
**mverganista@ua.pt*

Chemists have been challenged to replace the catalysts of noble metals based on Rh, Ru, Ir, Pt and Pd with cheap and Earth-abundant metals like Fe, Cu, Co or Ni. From this last set, iron is a privileged metal since it is the second most abundant metal on the Earth's crust, is biocompatible and it has a wide range of oxidation states.[1] Iron heterogeneous catalysts are used in the industry in the production of syngas and ammonia, however, the development of homogenous iron catalysts has only been explored only in the last 15 years, determining a "new iron age".[2][3] Of the homogenous iron catalysts, a promising class are iron tricarbonyl cyclopentadienones, presenting a similar structure and catalytic activity to their ruthenium analogue, the Shvo pre-catalyst.[4]

Iron tricarbonyl cyclopentadienone complexes can be efficiently prepared by reacting alkynes with Fe(0) carbonyls. They can participate in a wide range of reactions such as hydrogenation, oxidation and hydrogen borrowing.[5] By modifying the substituents on the cyclopentadienone ring, we can shift the steric and electronic properties of the complex, which have a drastic influence on the catalytic activity.[6] In the literature, the most common substituents of the cyclopentadienone ring are (cyclo)alkyl, aryl and alkylsilanes.

We aim to use this class of complexes to catalyze the modification of polyols by hydrogen borrowing, which is normally performed in apolar solvents. The poor solubility of these substrates in apolar solvents impelled us to prepare water-soluble catalysts. In this contribution, we present the synthesis and characterization of novel iron cyclopentadienone complexes.

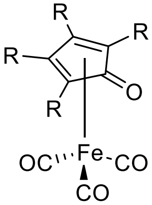

Figure 1: General structure of iron tricarbonyl cyclopentadienones

ACKNOWLEDGMENTS

This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020, UIDP/50006/2020, CEE-CINST/2018 and PTDC/QUI-QOR/1131/2020.

Funding

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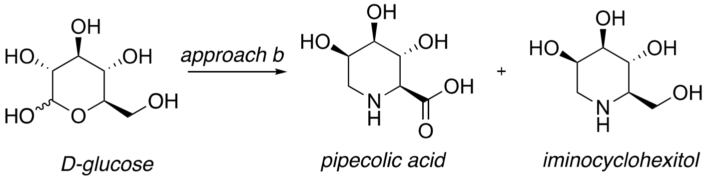
QO41

Divergent syntheses of iminocyclohexitols and polydroxylated pipecolic acids

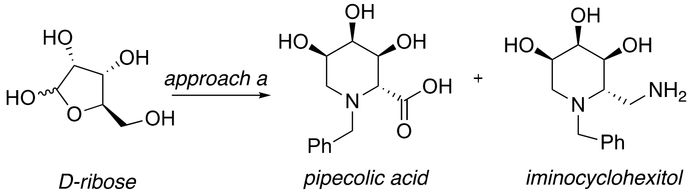
Ramón J. Estévez, **Rosalino Balo, Paula Martin, Pablo López,**
Andrés Fernández and Juan C. Estévez*

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares
and Departamento de Química Orgánica, Campus Vida, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, SPAIN.
juancarlos.estevez@usc.es

Carbohydrates are an abundant source of useful scaffolds for the stereoselective synthesis of functionalized carbo- and heterocycles.[1] Two approaches have been dessigned for this purpose. Thus, the new ring can be generated from an open chain carbohydrate derivative (*approach a*). The alternative approach (*approach b*) involves the generation of a bicyclic derivative constituted by the original sugar ring and a new ring, and the ulterior opening of the sugar ring. In recent times, the generation of the carbo- or heterocyclic ring has been approached by an inter- or intramolecular a double displacement of a sugar ditosylate, dimesylate, ditriflate or dibromide by a properly nucleophile. Specifically, the *approach b* has only been applied to the preparation of azetidine iminosugars [2] and tiosugars [3].
Here we report a new contribution to this field, which consists of two novel divergent syntheses of iminocyclitols and polyhydroxylated pipecolics acids, starting from D-glucose (Scheme 1) and from D-ribose (Scheme 2), respectively..



Scheme 1



Scheme 2

Acknowledgements
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Squaraine dyes derived from benz[*e*]indole as fluorescent probes for human serum albumin detection and quantification

Lucinda V. Reis[1*], Eurico Lima[1,2] , Margarida A. Sousa[1], Andreia G. Barroso[1], Renato E. Boto[2], Paulo Almeida[2]

[1]Chemistry Centre of Vila Real (CQ-VR), University of Tras-os-Montes and Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal

[2]Health Sciences Research Centre (CICS-UBI), University of Beira Interior, Av. Infante D. Henrique, 6201-506, Covilhã, Portugal
**lucinda.reis@utad.pt*

Human serum albumin (HSA) is considered the most abundant protein in human blood plasma [1], corresponding to approximately 60% of total plasma protein, and its concentration in serum and urine is an essential biomarker for the detection of cardiovascular diseases, diabetes, and kidney disease [2]. Therefore, when the concentration of this serum albumin is below 35 g/L, a condition called hypoalbuminemia arises, which is associated with several pathological conditions, such as malnutrition, rheumatoid arthritis, infection, and cancer [3-4].

In this work, we present the results obtained in the study of the interaction of the zwitterionic squaraine dye **1** and its functionalized derivatives with the picolyl- (**2**) and dipicolylamine (**3**) groups, with HSA by fluorescence in phosphate buffer (Fig. 1). The dyes, in the presence of HSA, presented values of quantum yields of fluorescence much higher than those presented in the absence of the protein, being dye **1** the one that presented the highest value (77%). We also calculated the detection and quantification limits, the method sensitivity, and the dye-protein binding constants for these dyes.

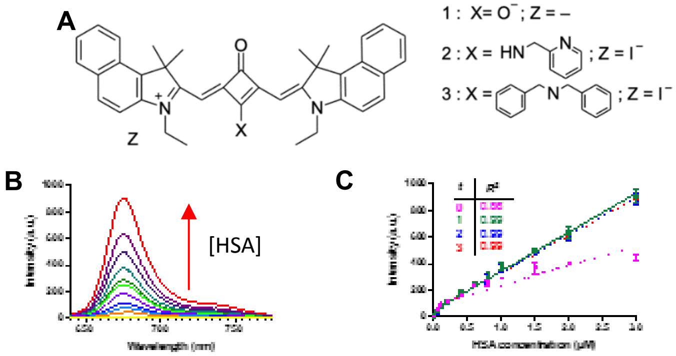

Fig.1. A: Structural formula of squaraine dyes **1**-**3**. **B**: Fluorescence emission spectra of dye **1** with increasing albumin concentrations. **C**: Linear regression graph of emitted dye **1** fluorescence intensity as a function of protein concentration at various dye-protein incubation times (*t* = 0, 1, 2, 3 h).

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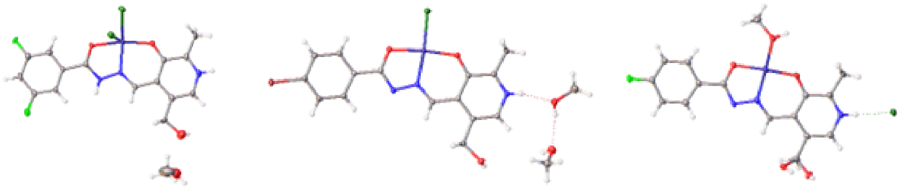
Study of the supramolecular self-assembly of Cu(II) complexes of pyridoxal derived ligands

Fernando Avecilla[1], **Lucía Ramos-Pan**[1], **Antía Sar-Rañó**[1], **Miguel Maestro**[1], **Josefina Méndez**[1], **Vanessa Valdiglesias**[1]

[1]Universidade da Coruña. Grupo NanoToxGen, Centro de Investigacións Científicas Avanzadas, As Carballeiras, s/n, San Vicenzo de Elviña 15008, A Coruña, España.
**fernando.avecilla@udc.es*

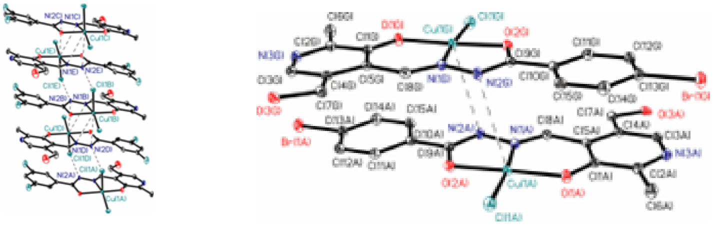
Copper(II) complexes from halogen hydrazones derived from pyridoxal were synthetized in methanol solution and characterized by MS, IR and single crystal X-ray diffraction. Compounds **1** and **3** are fluorine and compound **2** is a bromine derived. Fig.1 shows the structures obtained for these compounds, which present different environmental coordinates ligands and different coordination geometries.



a) b) c)

Fig.1. ORTEP of the asymmetric unit in the crystal structures of the compounds **1**(a), **2**(b) and **3**(c).

The coordination geometry around Cu(II) ion can be described as square-pyramid in compound **1**, and as square plane in compounds **2** and **3**. In compound **1**, the crystal packing shows a polymeric chain with a chlorine atom acting as an asymmetric bridge, through a hydrogen bond, between two complex units. A Cu···N pseudocoordination occupies the sixth position in the other side, bond distance, 3.502(2) Å. In compound **2**, dimers with Cu···N pseudocoordination in the fifth empty position and a bond distance of 3.338(2) Å is the predominant specie (see Fig.2). In compounds **3**, the methanol coordinated molecule causes that the crystal packing is marked by the hydrogen bonds interactions and a supramolecular network specie was isolated.



A B

Fig.2. Supramolecular dimers are interconnected through hydrogen bonds with chlorine atoms in compound **1**(A) and form isolated units in compound **2**(B) interacting by van der Waals forces.

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QUÍMICA Y SALUD

Synthesis, characterization and evaluation of the cytotoxic activity against A549 cell line of 2,6-diformyl-4-methylphenol hydrazones.

Antía Sar-Rañó[1,*], **Fernando Avecilla, Vanessa Valdiglesias, Natalia Fernández-Bertólez**

NanoToxGen group, Centro de Investigacións Científicas Avanzadas, As Carballeiras, s/n, San Vicenzo de Elviña 15008, A Coruña, España.
**antia.sar@udc.es*

Hydrazide-hydrazone compounds, especially those ones with aromatic rings, have shown many interesting properties in the pharmacological area. It has been demonstrated that different hydrazides and hydrazones have antimicrobial, analgesic, anti-inflammatory, antitubercular or antitumoral activity among other properties [1].

Six different hydrazide-hydrazones were synthesized from 2,6-diformyl-4-methylphenol and aromatic hydrazides [2]. After being isolated by crystallization, the compounds were characterized in solid state and in solution by NMR, MS, IR and single crystal X-ray diffraction. Figure 1 shows the structures obtained for some of the compounds.

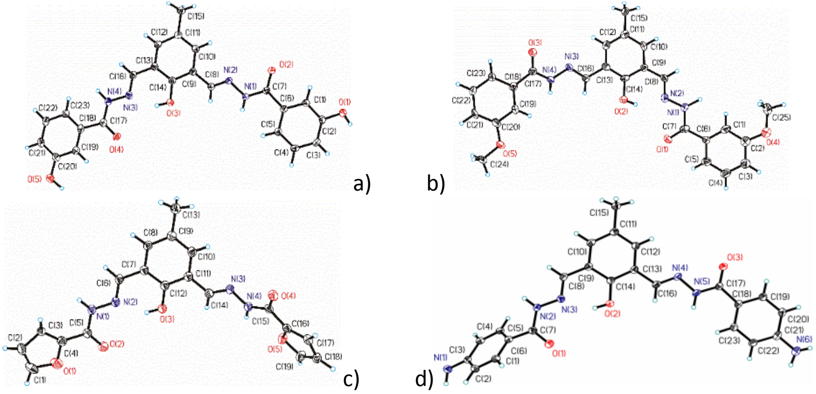

Fig.1. ORTEP diagram of the compounds a) H2 b) H3 c) H4 and d) H5.

Cytotoxicity of these compounds was tested on A549 cell line. The MTT assay was carried out in a range of concentrations from 0.1 to 500 µM and with different times of exposure (24 and 48 h). The IC_{50} values are very different comparing the compound and exposure times (see Table 1). The compound with the strongest activity for both times contains furan groups. After 48 h the hydrazide-hydrazones with the fluorobenzene, methoxybenzene and pyridine groups showed IC_{50} values, lower than 40 µM, while the compounds with hydroxybenzene and aminobenzene had IC_{50} values higher than 100 µM.

Table 1. IC_{50} values of 2,6-diformul-4-methilphenol hydrazones (µM).

	H1	H2	H3	H4	H5	H6
24h	-	186.04 ± 20.55	-	85.87 ± 3.53	185.35 ± 31.24	316.45 ± 58.87
48h	18.94 ± 2.87	112.01 ± 5.42	39.54 ± 6.97	15.48 ± 3.42	104.43 ± 11.30	32.41 ± 1.61

Acknowledgements

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Synthesis, characterization and DNA binding of a vanadium (V) complex derived from 2,6-diformyl-4-methylphenol.

Antía Sar-Rañó[1*], Fernando Avecilla[1], Iago Vázquez

[1]NanoToxGen group, Centro de Investigacións Científicas Avanzadas, As Carballeiras, s/n, San Vicenzo de Elviña 15008, A Coruña, España.
**antia.sar@udc.es*

Vanadium complexes have demonstrated very high potential as metallodrugs. Antitumour, antiparasitic, antiviral, antibacterial and insulin-mimetic activities are some of the properties that vanadium compounds can exhibit [1][2]. Therefore, the study of interaction between these compounds and some biological molecules such as DNA is really interesting.

A vanadium (V) complex was synthesized in methanol using VO(acac)$_2$ and a hydrazone ligand as reagents [3]. After the isolation of the compound it was characterized in solution and in solid state by NMR, MS, IR and single crystal X-ray diffraction. Figure 1 shows the structure of the obtained compound.

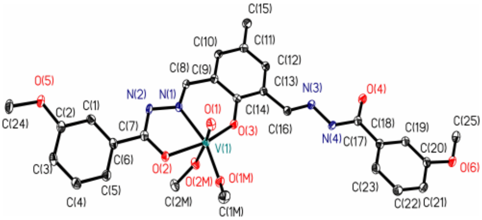

Fig.1. ORTEP diagram of the vanadium (V) complex.

The interaction between the vanadium complex and ct-DNA was studied by UV-vis spectroscopy after verifying that the compound was stable in phosphate buffered saline (pH = 7.4). The addition of increasing amounts of ct-DNA produce hypochromic and bathochromic effects on the complex´s spectra (see Figure 2). These results showed that the complex intercalated between the nitrogenous bases of DNA, interacting with them by p-p staking [4]. The interaction constant obtained by the Benesi-Hildebrand equation [5] has a value of $2.3 \cdot 10^3$ M^{-1}.

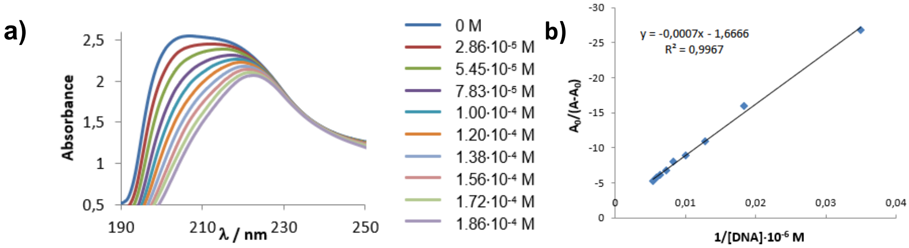

Fig.2. a) Spectra of the vanadium complex (49.3 µM) with different concentrations of ct-DNA (0-213 µM) in PBS solution (pH = 7.4) with 10% of ethanol. b) Plot of the Benesi-Hildebrand equation.

Acknowledgements

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Estudos sobre a síntese de novos heterociclos baseados na unidade de cromeno e purina

A. Sousa[1,*], D. Costa[1], M. Costa[2,3], M.F. Proença[1]

[1] Centro de Química, Campus de Gualtar, Universidade do Minho, 4710-057 Braga, Portugal
[2] Instituto de Ciências da Vida e da Saúde (ICVS), Escola de Medicina, Universidade do Minho, Campus de Gualtar, Braga, Portugal
[3] ICVS/3B's – PT Laboratório Associado, Braga/Guimarães, Portugal
**id9570@alunos.uminho.pt*

O núcleo de cromeno, tal como o de purina, constituem duas importantes classes de compostos e tem sido realizado um extenso trabalho na síntese de novos derivados de cada uma destas famílias, para serem estudados como potenciais fármacos. Estas unidades estão presentes em diversos compostos de origem sintética e natural que exibem propriedades biológicas e farmacológicas importantes, incluindo atividade anticancerígena.[1][2]

No grupo de investigação, foi possível gerar derivados de 3-(6-amino-9*H*-purin-2-il)-2*H*-cromeno (Fig.1), combinando na mesma molécula a unidade de cromeno e de adenina. Estes compostos foram preparados por reação de um salicilaldeído com um composto de metileno ativado, mas o produto foi sempre isolado com rendimentos moderados a baixos. Foi proposto um mecanismo para a sua formação, envolvendo a reação entre um 3-ciano-2-oxocromeno e um derivado de imidazole.

Com base nesta proposta, foram realizados estudos de reatividade envolvendo compostos modelo contendo os núcleos de oxocromeno e de imidazole, de forma a confirmar o mecanismo proposto e assim poder otimizar as condições de preparação destes derivados de 3-(6-amino-9*H*-purin-2-il)-2*H*-cromeno com potencial atividade anticancerígena e ampliar a diversidade de substituintes.

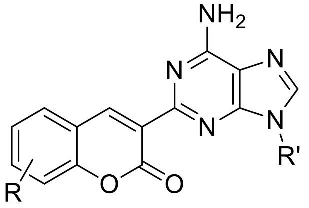

Fig.1. Derivados de 3-(6-amino-9*H*-purin-2-il)-2*H*-cromeno.

Agradecimientos

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QS53

Fighting bacterial infections: antimicrobial peptides and ionic liquids

A. R. Ferreira[1], A. Gomes[1], M. Ferreira[1], C. Nunes[2], C. Teixeira[1], S. Reis[2], P. Gomes[1] and P. Gameiro[1,*]

[1]LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, LAQV-REQUIMTE, 4169-007 Porto, Portugal.
[2]LAQV-REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Porto 4050-313, Portugal.
**agsantos@fc.up.pt*

Antimicrobial peptides (AMPs) and ionic liquids (ILs) represent attractive classes of molecules to fight multi-drug resistant (MDR) bacteria. AMPs are typically cationic and amphipathic, and display a membrane-targeting activity, with a fast-killing kinetics, being less prone to induce mechanisms of resistance. ILs are composed of organic cations and organic/inorganic anions with melting temperatures usually below 100 ºC, which are being widely explored in the pharmaceutical field to improve drug solubility, to rescue old drugs, or as antimicrobial agents. We propose an AMP-based strategy based on covalent and non-covalent conjugation of AMPs with alkylimidazolium bromide ILs, aiming at boosting the therapeutic potential of AMPs. Herein, BP100 and W-BP100 [1]. AMPs were combined with imidazolium-based ILs with a 12-carbon alkyl chain, reported to have antibacterial and antibiofilm properties, by covalent conjugation using click chemistry [2] and by non-covalent conjugation (equimolar mixtures). The antibacterial and cytotoxicity activities of AMP-IL conjugates and their correlation with model membranes of bacteria and eukaryotic cells using biophysical tools will be demonstrated. A preliminary study on the effect of the most promising peptide, W-BP100, on aggregation and fusion of negatively charged giant unilamellar vesicles (GUVs) using confocal microscopy will be presented.

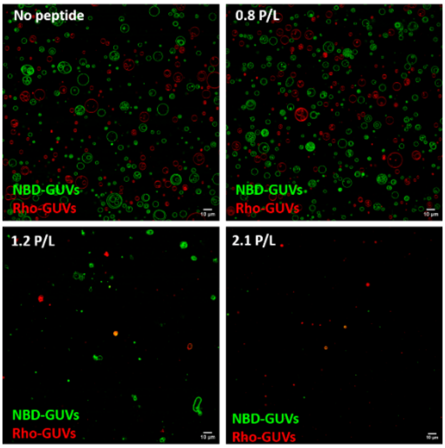

Fig.1. Effect of W-BP100 on the fusion of POPC:POPG (1:1) GUVs labelled with 2% NBD-DPPE or 0.1% Rho-DPPE (P/L = 0.8, 1.2 and 2.1) and mixed at 1:1 ratio, upon 10 min incubation, using confocal microscopy. Scale bar: 10 µm.

Agradecimientos

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Study of new derivatives based on coelenterazine for photodynamic therapy

Daiane N. Maronde[1*], Ivo E. Sampaio-Dias[1], Luís Pinto da Silva[2], Leandro M. O. Lourenço[3], and José E. Rodríguez-Borges[1]

[1] LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2] Chemistry Research Unit (CIQUP), Institute of Molecular Sciences (IMS), Department of Geosciences, Environment and Territorial Planning, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[3] LAQV/REQUIMTE and Department of Chemistry, University of Aveiro, Universidade de Aveiro, 3810-193 Aveiro, Portugal.
**dnascimentomaronde@gmail.com*

Nowadays, the cancer treatment still is a big challenge, therefore being one of the causes of death in the world. Furthermore, traditional methods of treatment are invasive and/or cause secondary harm to patients [1]. In this context, photodynamic therapy (PDT) appears as an efficient alternative for its treatment. This therapy combines a photosensitizing drug, visible light, and molecular oxygen ($^3O_2$) to generate reactive oxygen species (ROS), mainly singlet oxygen ($^1O_2$), which is cytotoxic for cancer cells [2,3].

Recent studies show that analogues of Coelenterazine (Clz) compounds have shown relevant cell-selective toxicity in different cancer cell lines, such as breast, liver, prostate, and neuroblastoma, without cytotoxic effects in corresponding non-tumoral cells at the same concentrations [4]. Based on these results, this work aims to synthesize a new series of Clz-based PS derived from pyrazine scaffold, a common precursor in the synthesis of Clz and its structure-related analogues.

In this work is disclosed the synthesis of precursors, with high chemical yields, for the assembly of Clz analogues. Currently, these compounds are being studied for the assembly of new PS with potential application in PDT.

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QS55

Discovery of Neuroprotective Hits Using 2-Azanorbornane as a Constrained Proline Surrogate in Glypromate Neuropeptide

Ivo E. Sampaio-Dias[1,*], Sara C. Silva-Reis[1], Miguel Santejo[2], Márcia A. Liz[2], Xerardo García-Mera[3], José E. Rodríguez-Borges[1]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2]Neurodegeneration Team, Nerve Regeneration Group, IBMC – Instituto de Biologia Molecular e Celular, Universidade do Porto, Portugal, and i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Rua Alfredo Allen 208, 4200-135 Porto, Portugal.
[3]Department of Organic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Praza do Seminario de Estudos Galegos, 15705 Santiago de Compostela, Spain.
**idias@fc.up.pt*

Alzheimer's and Parkinson's diseases are neurodegenerative disorders of the central nervous system that affect millions of people worldwide without curative treatments currently available.[1] In this sense, the research on neuroprotective drugs is considered a health priority.

Glypromate (**Fig.1**) is a neuroprotective tripeptide found in brain tissue and it is obtained by the *N*-terminal cleavage of insulin-like growth factor 1. Although its *modus operandi* remains unknown, *in vitro*, and *in vivo* studies have demonstrated its neuroprotective activity against several neurotoxic agents. However, this neuropeptide exhibits low gastrointestinal absorption and susceptibility towards enzymatic degradation. To overcome these unfavorable pharmacokinetic properties, constrained proline mimetics of this neuropeptide have emerged as a successful strategy, and additionally providing analogs with improved neuroprotective profiles.[1]

In this work, the design, synthesis, and biological evaluation of a new series of Glypromate peptidomimetics using 2-azanorbornane as a proline surrogate is disclosed.[1] Following an innovative one-pot synthesis approach, four new constrained Glypromate analogues (**Fig.1**) were successfully in excellent global yields starting from 2-azanorbornane scaffold (75-84%).[1] Neuroprotective assays performed in differentiated SH-SY5Y cells using 6-hydroxydopamine (6-OHDA) as stress inducer showed that all these peptidomimetics exhibited superior percentage of recovery (29.7-40.0%) than the parent neuropeptide (12.8%) at 100 μM after 6-OHDA injury.[1]

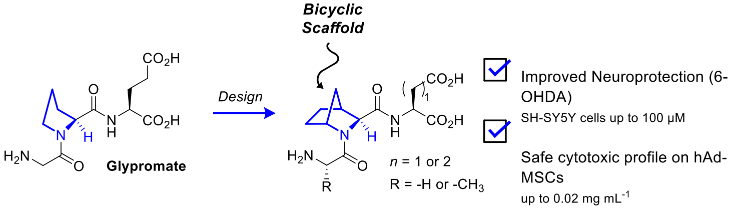

Fig.1. Glypromate and 2-azanorbornane-based analogs with improved neuroprotective activity.

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Design, Synthesis, and Biological Evaluation of Glypromate-Based Neuroprotective Conjugates with Pharmaceutical Active Ingredients

Sara C. Silva-Reis[1,2,*], Ivo E. Sampaio-Dias[1], Hugo F. Costa-Almeida[1], Xavier C. Correia[1], Vera M. Costa[2,3], Xerardo García-Mera[4], José E. Rodríguez-Borges[1]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
[2]UCIBIO/REQUIMTE, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[3]Associate Laboratory i4HB – Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4] Department of Organic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Praza do Seminario de Estudos Galegos, 15705 Santiago de Compostela, Spain.
**sarac.silva-reis@hotmail.com*

The main neurodegenerative disorders of central nervous system, affecting millions of people worldwide, are Alzheimer (AD) and Parkinson (PD) diseases. The absence of effective therapies to treat and slow down the progression of these neurodegenerative processes constitutes a serious medical concern.[1] In this sense, the development of new neuroprotective therapies becomes imperative.

Glypromate is an endogenous short neuropeptide with the sequence of Gly-Pro-Glu, displaying neuroprotective activity in many *in vitro* models of AD and PD. Despite its neuroprotective potential, this neuropeptide exhibits low biochemical stability towards enzymatic proteolysis and reduced blood-brain barrier permeability.

The use of constrained proline mimetics and capping strategies have been employed in the assembly of bioactive Glypromate analogues with improved lipophilicity and enhanced enzymatic stability.[2] NeuroPro project aims at the design, synthesis, and biological evaluation of novel constrained Glypromate analogues by exploring the chemical conjugation of these peptidomimetics with relevant active pharmaceutical ingredients (API) used in AD and PD therapies. This approach is expected to deliver new neuroprotective hits with higher metabolic resistance while exploring synergism between Glypromate analogues and API.

In this work, the assembly of 54 new Glypromate conjugates with Amantadine, Memantine, and Aminoindane is disclosed. These peptide-conjugates are currently undergoing biological evaluation to assess their cytotoxicity in human differentiated SH-SY5Y cells. The conjugates with the lowest cytotoxicity profiles will be selected to proceed with *in vitro* neuroprotection studies.

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QS57

Fluoroquinolone metalloantibiotics: fighting *Staphylococcus aureus* infections

M. Ferreira[1,*], B. Ribeiro[1] and P. Gameiro[1]

[1] LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
**mariana.ferreira@fc.up.pt*

Fluoroquinolones (FQs) are antibiotics extensively used in the clinical practice due to the broad spectrum of action, although several bacterial resistance mechanisms are reported against this family of antibiotics. Our strategy to bypass bacterial resistance mechanisms developed against FQs is their complexation with copper and phenanthroline (phen). These metalloantibiotics of CuFQphen have been widely studied, being known that are very stable under physiological conditions and exhibit antibacterial activity [1]. Metalloantibiotics revealed an improved antimicrobial activity compared to FQs against several clinical isolates, especially against methicillin-resistant *Staphylococcus aureus* (MRSA) [2].

In this work [3], a biophysical study focused on the interactions of metalloantibiotics with membranes of *S. aureus* was carried out. Different mimetic lipidic systems - liposomes of POPG, POPG/(16:0)CL, and (18:1)DAG/(16:0)CL/POPG - were chosen to mimic the membrane of *S. aureus*, and further characterized by fluorescence anisotropy (r) of DPH probe – transition temperatures were assessed. The partition constants of FQs and metalloantibiotics were determined in the three mimetic systems, by steady-state fluorescence spectroscopy. The membrane fluidity of some MRSA clinical isolates was evaluated through the study of the generalized polarization (GP) of Laurdan, in the absence and presence of FQs and metalloantibiotics.

Partition results evidenced a larger interaction of the metalloantibiotics with the mimetic systems of *S. aureus* and their presence proved to induce clear changes on the membrane fluidity of MRSA. Biophysical assays provided useful information about the interaction of metalloantibiotics with bacterial membranes, complementing the microbiological outcomes previously obtained.

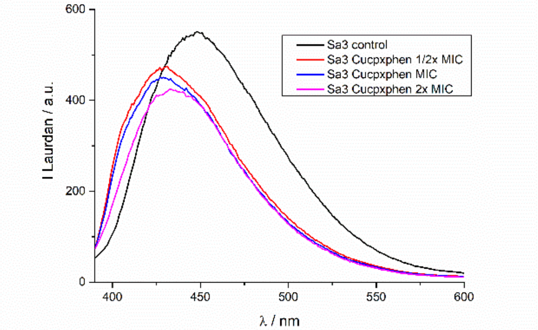

Fig.1. Fluorescence emission spectra of Laurdan-labeled MRSA clinical isolates (Sa3) in the absence (control) and presence of increasing concentrations (1/2x MIC, MIC and 2x MIC) of Cucpxphen metalloantibiotic, from [3]. MIC is the minimum inhibitory concentration.

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QS58

BDDE, a marine bioactive metabolite, as inspiration for the synthesis of chalcone derivatives to fight antimicrobial resistance

Ana Jesus [1,2,▯], Fernando Durães [1,2,▯], Nikoletta Szemerédi [3], Joana Freitas-Silva [2,4], Paulo Martins Costa [2,4], Eugénia Pinto [2,5], Madalena Pinto [1,2], Gabriella Spengler [3], Emília Sousa [1,2,*], Honorina Cidade[1,2,*]

[1] Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal;
[2] CIIMAR—Interdisciplinary Centre of Marine and Environmental Research, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal;
[3] Department of Medical Microbiology, Albert Szent-Györgyi Health Center and Albert Szent-Györgyi Medical School, University of Szeged, Semmelweis utca 6, 6725 Szeged, Hungary
[4] ICBAS—Institute of Biomedical Sciences Abel Salazar, University of Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[5] Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
▯These authors contributed equally to this work.
** esousa@ff.up.pt and * hcidade@ff.up.pt*

Antibiotic resistance is a global public health issue that threatens human population worldwide, being one of the topics that arouse the attention of several research groups [1]. There are many mechanisms related to this phenomenon, such as inhibition of biofilm formation, impermeabilization of cellular membrane, target modification, and drug inactivation, and extrusion through efflux pumps (EPs) [2]. Therefore, the development of new compounds capable to revert this situation is urgent, either as new antimicrobial compounds and/or as agents that potentiate the antimicrobial response of the existent drugs.

Terrestrial and marine natural products have been in the spotlight regarding the discovery of new drugs, especially antibacterial and antifungal compounds [3]. Chalcones are a class of flavonoids that have been extensively reported for their biological activities, including antimicrobial activity [4]. Interestingly, some brominated chalcones as well as other marine-derived brominated metabolites have been reported for exhibiting antibacterial activity [5].

Herein, bis-(3-bromo-4,5-dihydroxybenzylether (BDDE), a macroalgae brominated bromophenol that demonstrated interesting antimicrobial activity [6], was used as model for the synthesis of a series of 18 chalcones derivatives, including seven chalcones and their reduced derivatives, dihydrochalcones and diarylpropanes. All the derivatives were accessed regarding to their antibacterial and antifungal activities.

Dihydrochalcones and diarylpropanes exhibited inhibitory action towards the biofilm formation by the methicillin- and oxacillin-resistant *S. aureus* 272123, and displayed inhibition of EPs in the same strain, which suggests that these compounds are EP inhibitors. Among all the compounds, two chalcones showed antifungal activity against a clinical strain of *Trichophyton rubrum*, and all the derivatives demonstrate ability to reverse the antibiotic resistance to vancomycin in the resistant *Enterococcus faecalis* B3/101 strain. The reduced derivatives, dihydrochalcones and diarylpropanes, also did not present cytotoxicity in NIH/3T3 cell line. The overall results suggest that some synthetized chalcone derivatives could be used as potential antibacterial adjuvants, as hits for the inhibition of EPs.

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Point-of-care determination of calcium in saliva using a developed microfluidic paper-based analytical device

Juliana I. S. Aguiar*, **Mafalda T. S. Silva, António O. S. S. Rangel, Raquel B. R. Mesquita**

Universidade Católica Portuguesa, CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 137, 4169-005, Porto, Portugal
*jiaguiar@ucp.pt

Calcium is a divalent cation present in saliva that plays a critical role in numerous body functions such as skeletal mineralization, signal transduction, nerve conduction, muscle contraction, and blood coagulation. The determination of calcium concentration may anticipate potential problems or help to improve target therapies.

This work presents a new and simple microfluidic paper-based analytical device (μPAD) for calcium determination in saliva samples. This μPAD analytical method is based on the colorimetric reaction between calcium and cresolphthalein complexone (CPC). According to the design principle, saliva samples move through paper channels, composed by two layers of paper discs, and form a strongly and intense purple colour product in the reagent layer. The colour product formed is more intense with an increasing calcium concentration and was measured by image processing after digital scanning. Under the optimal conditions, the paper device was enabled to determine calcium in the 0.10 – 4.0 mmol/L analytical range with detection and quantification limits of 0.085 and 0.028 mmol/L, respectively. The μPAD sensitivity was stable for up 2 weeks when stored in vacuum conditions. The accuracy of the developed method was established by analysing saliva samples (#10) with the developed μPAD and with the atomic absorption spectrometry method (AAS). The relative deviation between the two sets of results was below 10%.

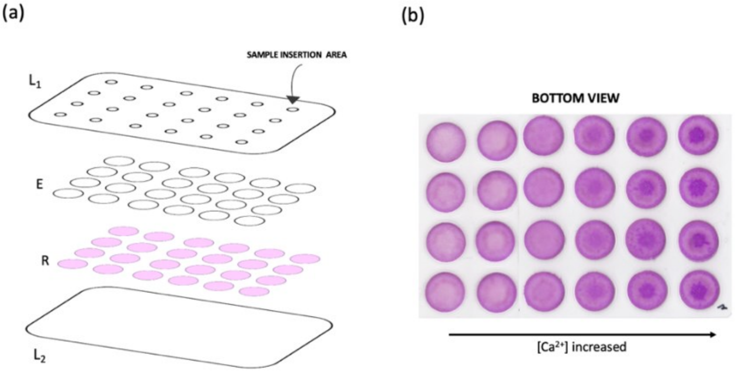

Fig. 1. Schematic representation of the μPAD assembly for calcium determination; (a) the paper discs alignment and the respective layers: L_1 and L_2, laminating pouches sheets; E, empty layer; R, reagent layer; (b) Real image of the bottom view of the μPAD after placing the standard solutions.

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Cromeno[2,3-*b*]piridinas: síntese e avaliação do potencial anticancerígeno para o cancro da mama

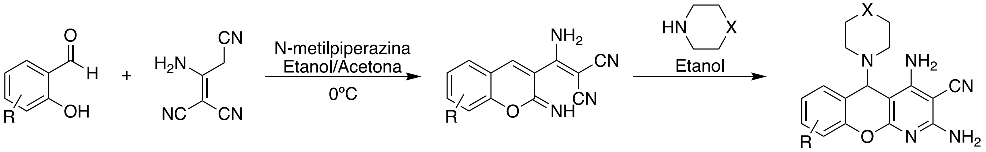
Diogo Lopes[1,*], Marta Costa[2,3], Sofia Oliveira-Pinto[2,3], Olívia Pontes[2,3], Luísa Carvalho[2,3], Fátima Baltazar[2,3], Fernanda Proença[1]

[1]Departamento de Química, Universidade do Minho, Campus de Gualtar, Braga, Portugal
[2]Life and Health Sciences Research Institute (ICVS), Universidade do Minho, Campus de Gualtar, Braga, Portugal
[3]ICVS/3B's - PT Government Associate Laboratory, Braga/Guimarães, Portugal
**diogoavl1994@gmail.com*

Os derivados de cromeno têm sido identificados como agentes anticancerígenos, atuando em diversos alvos moleculares envolvidos na progressão do cancro.[1,2] Cromeno[2,3-*b*]piridinas foram igualmente consideradas estruturas com atividade biológica promissora e no grupo foram já sintetizados vários derivados, a partir de salicilaldeídos.

Neste trabalho irá ser discutida a reação de diferentes salicilaldeídos com 2-amino-1,1,3-tricianopropeno, na presença de *N*-metilpiperazina, que permitiu gerar 2-imino-2*H*-cromenos.[3] A evolução para as cromeno[2,3-*b*]piridinas correspondentes ocorreu em etanol, na presença de diferentes piperazinas (Esquema 1).[4]

A atividade anticancerígena de uma seleção de cromeno[2,3-*b]*piridinas foi testada em linhas celulares do cancro da mama (MCF-7, Hs578t e MDA-MB-231). Foi também avaliada a sua toxicidade na linha celular não neoplásica MCF-10A, o que permitiu concluir que os compostos mais ativos apresentam um perfil seletivo para as células malignas. Foram identificados três derivados de cromeno[2,3-*b*]piridina bastantes promissores, com valores de IC_{50} baixos na gama dos micromolar e com a capacidade de inibir a proliferação celular, induzir a paragem do ciclo celular e a apoptose.[4]



Esquema 1. Reação de síntese dos 2-imino-2*H*-cromenos e das cromeno[2,3-*b*]piridinas.

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Indoor levels of fine and ultrafine particles at Portuguese fire stations

Joana Teixeira, Gabriel Sousa, Cristina Delerue-Matos, Simone Morais, Marta Oliveira*

REQUIMTE/LAQV-Instituto Superior de Engenharia, Instituto Politécnico do Porto, R. Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal
** E-mail: marta.oliveira@graq.isep.ipp.pt*

About 7 million people per year die from air pollution-related diseases. Particulate matter (PM) is a widespread air pollutant consisting of a mixture of solid and liquid particles suspended in the air. PM is classified according to the aerodynamic diameter in coarse, fine, and ultrafine particles (PM> 2.5 µm, PM≤ 2.5 µm, and PM≤ 0.1 µm, respectively) [1]. Occupational exposure as a firefighter was recently classified by the International Agency for Research on Cancer as carcinogenic to humans due to sufficient evidence for the development of mesothelioma and bladder cancer [2]. Firefighters are regularly exposed to health-relevant pollutants released from fires including PM [2, 3]. So far, information about firefighters' exposure to PM, mainly to fine and ultrafine particles remains almost inexistent [4, 5]. This work characterizes the levels of coarse, fine, and ultrafine PM in different indoor environments of Portuguese fire stations: firefighting vehicles garage, PPE storage room, bar, and a common area.

PM fractions were collected with a DEKATI low-pressure impactor (DLPI+, Dekati®, Finland) at an outlet pressure of 40 mbar and a flow rate of 9.96 L/min. Coarse (PM_{10}, $PM_{5.4}$, $PM_{3.6}$ µm), fine ($PM_{2.5}$, $PM_{1.6}$, $PM_{0.95}$, $PM_{0.60}$, $PM_{0.38}$, $PM_{0.26}$, $PM_{0.16}$ µm) and ultrafine PM fractions (PM_{95}, PM_{54}, and PM_{31} nm) were daily sampled over a regular work week at 7 fire stations from the district of Porto, Portugal.

The total PM cumulative concentrations ranged between 4.55 to 8.37 mg/Nm^3, with maximum values reaching 16.44 mg/Nm^3. At some fire stations, levels of total cumulative PM were higher than the guideline defined by OSHA, 5.0 mg/m^3, for respirable particles [8]. Cumulative levels of fine (0.87-10.49 mg/Nm^3), and ultrafine (0.17 – 3.83 mg/Nm^3) PM accounted for 59.1 – 69.6 and 17.6 – 23.6% of total PM, respectively. The highest median levels were observed in the bar (5.93 mg/Nm^3) and the PPE storage room (5.70 mg/Nm^3), followed by the common area (5.58 mg/Nm^3) and the garage where firefighting vehicles are parked on (5.30 mg/Nm^3). Non-cumulative levels of $PM_{2.5}$ (251 - 686 µg/Nm^3) and PM_{10} (24 - 109 µg/Nm^3) found in the indoor air of Portuguese fire stations exceeded the available national and international indoor air quality guidelines (25 µg/m^3 and 50 µg/m^3, respectively) [6, 7]. Further studies focusing in the inorganic and organic composition of fine and ultrafine PM should be addressed.

Funding

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Towards the "greenness" of a chemical synthesis of a new antifouling compound

Sara Godinho[1,2], Ana Laura Dias[1,2], Sara Cravo[1,2], José X. Soares[1,3], Madalena Pinto[1,2], Carlos M. M. Afonso[1,2] and Marta Correia-da-Silva[1,2*]

[1]Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal
[2]Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR/CIMAR), Porto, Portugal
[3]LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal.
*m_correiadasilva@ff.up.pt; dedicated by the author to the memory of Professor Costa Lima

In a previous research project of our group, a gallic acid (GA) derivative – GBA26 – was synthesized and revealed to be a highly promising eco-friendly antifouling (AF) agent [1-3]. Even though its 2-step synthesis from trimethylgallic acid, with an overall yield of 70%, the synthetic route wasn't environmentally safe, mainly due to the dificulties of management and toxicity associated with the use of TBTU amine coupling reagent and the deprotection step with BBr_3 [2]. The aim of this work was to optimize the previous synthesis to comply with the Twelve Principles of Green Chemistry, namely, use of eco-friendly solvents, replacement of hazards reagents, and reduce waste. GA was selected as the starting material as it can be extracted from grape wastes through green methodologies, making use of renewable feedstocks and allowing waste valorization. In the new synthetic pathway GA was first chemically protected with benzyl groups, followed by COMU-mediated amine coupling and hereafter by respective deprotection with Pd/C. Eventhough the increased number of steps (2 to 5), the overall yield of the new method was similar to the previous methodology. Green chemistry metrics were calculated to compare both synthetic pathways, namely atom economy (AE), reaction mass economy (REA), mass intensity (MI), and mass productivity (MP). While, the first refered method presented more favorable green metrics, the new method clearly uses safer chemistry and chemicals. Furthermore, with this new synthetic pathway, three intermediates were sucessfully purified by crystallization without the need of column chromatography, need in the purification of the intermediate of the previous method.

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SYNTHESIS OF NEW SURFACE-ACTIVE IONIC LIQUIDS DERIVED FROM ANTIMALARIAL DRUGS AND BILE ACIDS

Ana Teresa Silva[1]*, Isabel Oliveira[2], Denise Duarte[3], Diana Moita[4], Miguel Prudêncio[4], Fátima Nogueira[3], Cátia Teixeira[1], Ricardo Ferraz[1,5], Eduardo F. Marques[2], and Paula Gomes[1]

[1]LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, P-4169-007 Porto, Portugal;
[2]CIQ-UP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, P-4169-007 Porto, Portugal;
[3]Global Health and Tropical Medicine, Instituto de Higiene e Medicina Tropical, Universidade Nova de Lisboa, P-1349-008 Lisboa, Portugal;
[4]Instituto de Medicina Molecular, Faculdade de Medicina Universidade de Lisboa, P-1649 028 Lisboa, Portugal;
[5]Ciências Químicas e das Biomoléculas, Escola Superior de Saúde - Instituto Politécnico do Porto, P-4200-072 Porto, Portugal
*up201303026@edu.fc.up.pt

Malaria is a parasitic disease that occurs mostly in low-income countries, thus its containment or, ultimately, eradication demands new methodologies and synthetic strategies that are simple and inexpensive. Ionic liquids (ILs) may assume a prominent role in this scenario, as they are catching the attention of the Medicinal Chemistry community owing to their intrinsic biological activity and affordable synthesis through straightforward methods. [1-4] In this context, our focus consists of using an acid-base reaction between basic antimalarial aminoquinolines, such as chloroquine and primaquine, and natural amphiphilic acids, such as fatty and bile acids. The resulting ILs are expected to preserve the parent aminoquinolines' antimalarial action, while retaining the surface activity of the parent amphiphilic acids, thus facilitating the permeation of the whole IL structure through important biological barriers. In other words, our aim is to develop surface-active ionic liquids (SAILs) with intrinsic antimalarial properties. Results obtained thus far will be presented, demonstrating that SAILs can be produced which are active against different stages of malaria parasite development in the human host. Self-aggregation properties of these SAILs are currently under investigation and will be timely reported.

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Synthetic triazole compounds as potential inhibitors of SARS-CoV-2 attachment into host cells

Francisca Carvalhal[1-4], Rita Rebelo[3-5], Ana C. Magalhães[3,4,6], Cristina P. R. Xavier[3,4], Luísa Pereira[3,4], M. Helena Vasconcelos[3-5], Emília Sousa[1,2], Marta Correia da Silva[1,2*]

[1]Departamento de Ciências Químicas, Laboratório de Química Orgânica e Farmacêutica, Faculdade de Farmácia, Universidade do Porto (FFUP), Porto, Portugal.
[2]CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, Matosinhos, Portugal.
[3]i3S – Instituto de Investigação e Inovação em Saúde, UP, Porto, Portugal.
[4]IPATIMUP – Institute of Molecular Pathology and Immunology of the UP, Porto, Portugal.
[5] Departamento de Ciências Biológicas, Laboratório de Microbiologia, FFUP, Porto, Portugal.
[6]ICBAS–Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto
**E-mail:* m_correiadasilva@ff.up.pt; dedicated by the author to the memory of Professor Costa Lima

Click chemistry reactions are advantageous in organic synthesis, due to good yields, low by-products formation, selectivity, and simplicity. There is a wide range of applications for click chemistry in several major technological areas including drug discovery, combinatorial chemistry, material chemistry, bio-conjugation reactions, carbohydrate chemistry, and many others [1]. This is a copper-catalysed alkyne-azide cycloaddition type of reaction that originates a triazole linked derivative of the original compounds [2] (**Figure 1**).

Triazole compounds have been described as potential antiviral agents against different viruses, including coronavirus [3]. Angiotensin-converting enzyme (ACE2) was identified as the key human cellular host receptor for the attachment and entry of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) [4]. Virtual [5] and *in vitro* studies [3], as well as case studies [6], suggest that inhibiting the interaction between SARS-CoV-2 spike protein and ACE2 could possibly decrease the rate of viral infection.

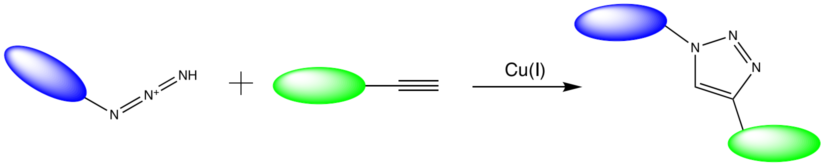

Figure 1. Click chemistry.

In this work, we selected three virtual hit compounds obtained by click chemistry for cell culture studies. The main goal was to understand their impact on: i) ACE2 host cell target expression and cellular toxicity; ii) SARS-CoV-2 cell infection. Their effect on cell infection was studied by immunofluorescence detection of SARS-CoV-2 spike protein levels in the Vero CCL-81 cells infected with this virus. Results showed that two compounds exhibited promising results inhibiting viral infection, with EC50 values around 32 μM, and did not present relevant toxicity at those concentrations, either to the Vero CCL-81 cells or to the human A549 tumor lung cells.

Acknowledgments

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Synthesis and *in vitro* evaluation *of versatile cell-penetrating* mitochondriotropic antioxidants

Sofia Benfeito[1*], **Carlos Fernandes**[1], **Daniel Chavarria**[1], **Sandra Barreiro**[1,2,3], **Fernando Cagide**[1], **Cátia Silva**[1], **José Teixeira**[4], **Renata Silva**[2,3], **Fernando Remião**[2,3], **Paulo J. Oliveira**[4], **Eugénio Uriarte**[5,6], **Fernanda Borges**[1]

[1] CIQUP-IMS – Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, R. Campo Alegre s/n, 4169-007 Porto, Portugal.
[2] Associate Laboratory i4HB – Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[3] UCIBIO – Applied Molecular Biosciences Unit, REQUIMTE, Laboratory of Toxicology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4] CNC – Center for Neuroscience and Cell Biology, CIBB - Centre for Innovative Biomedicine and Biotechnology, University of Coimbra, 3004-504 Coimbra, Portugal
[5] Departamento Química Orgánica, Facultad de Farmacia, Universidad de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain.
** ester.benfeito@fc.up.pt*

Targeting mitochondrial oxidative stress by using mitochondriotropic antioxidants based on the delocalized lipophilic triphenylphosphonium (TPP^+) cation appears an effective therapeutic solution for age-related disorders. However, TPP^+-based derivatives have shown cytotoxicity in several biological in vitro models, restricting their use for drug development. We observed that Mito.TPP, a derivative of dietary caffeic acid covalently linked to TPP by a 10-carbon alkyl chain (Fig.1), is cytotoxic to both human neuronal (SH-SY5Y) and hepatic (HepG2) cells, increasing oxidative stress, decreasing intracellular ATP levels, leading to mitochondrial membrane depolarization and reduced mitochondrial mass after 24 h exposure. In a continuing effort to improve the performance of mitochondriotropic antioxidants based on a caffeic acid, a new set of mitochondria-targeted antioxidants were designed and synthesized, in which the TPP moiety was replaced by nitrogen-derived cationic carriers. As opposed to Mito.TPP, the novel compounds were not cytotoxic to SH-SY5Y and HepG2 cells up to 50 µM and after 24 h of incubation. All the cationic derivatives accumulated inside the mitochondria matrix and acted as neuroprotective agents against iron(III), hydrogen peroxide and tert-butyl hydroperoxide insults. Overall, the nitrogen-based cationic carriers can modulate the biological performance of mitochondria-directed antioxidants and a superior alternative to TPP^+.
The obtained data will be presented in this communication.

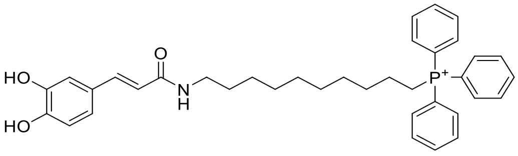

Fig.1. Chemical structure of Mito.TPP

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Tailoring VAS2870 scaffold to develop new covalent NOX2 inhibitors

Mariana Castelôa[1,*], Pedro Soares[1], Sofia Benfeito[1], Carla Lima[1], Fernanda Borges[1], Daniel Chavarria[1]

[1]CIQUP-IMS/Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto,
Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
** mariana15cas@gmail.com*

Neuroinflammation consists of an inflammatory response within the brain tissue that contributes to development and progression of neurodegenerative diseases (NDs). Nicotinamide adenine dinucleotide phosphate (NADPH) oxidase 2 (NOX2) catalyses the formation of reactive oxygen species (ROS) [1]. NOX2 is the main NOX isoform present in the brain and emerged as a potential drug target to reduce neuroinflammation [1]. Several molecules have been identified as NOX inhibitors (e.g.: apocynin, diphenyleneiodonium chloride, GSK2795039, VAS2870). However, they usually lack isoform selectivity and present assay-interfering effects, unfavourable drug-like properties, and/or cytotoxicity [2]. Therefore, there is an urgent need of selective and non-interfering NOX2 inhibitors to validate NOX2 as a potential therapeutic target for NDs and to clearly understand the enzyme's biological role [2].

VAS2870 is a non-selective, non-interfering NOX inhibitor that binds covalently to a conserved cysteine residue present in NOX dehydrogenase domain [2]. Taking advantage of the mechanism of action of VAS2870, the main objective of this work is the rational design and synthesis of a new library of VAS2870-based targeted covalent inhibitors for NOX2 (**Fig. 1**).

A synthetic strategy was designed and optimized to obtain a small library of VAS2870 derivatives. In addition, the ability of compounds to react with cysteine residues was evaluated by nuclear magnetic resonance (NMR). The results obtained so far will be presented in this communication.

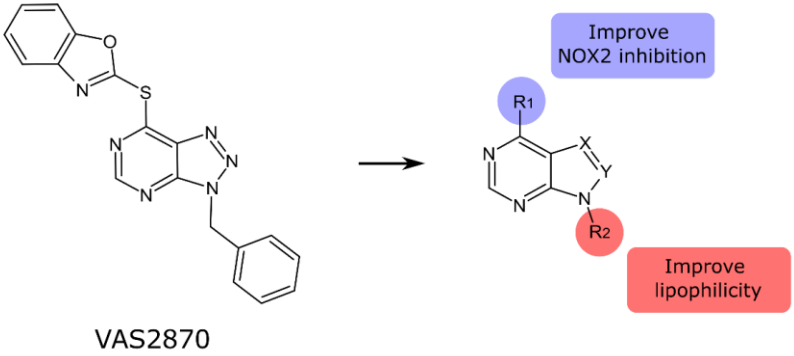

Fig.1. Chemical structure of VAS2870 and rational design of VAS derivatives for NOX2 inhibition.

Acknowledgements
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Fiscalins: a new source of substance P antagonists?

Márcia S. Martins[1,2], **Solida Long**[3], **Ana Jesus**[4,5], **Honorina Cidade**[1,2], **Madalena M. M. Pinto**[1,2], **Isabel F. Almeida**[4,5], **Maria T. Cruz**[6,7], **Emília Sousa**[1,2*]

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[2]CIIMAR–Interdisciplinary Centre of Marine and Environmental Research, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos, Portugal
[3]Department of Bioengineering, Royal University of Phnom Penh, Russian confederation Blvd., Phnom Penh 12156, Cambodia
[4]UCIBIO—Applied Molecular Biosciences Unit, MedTech, Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[5]Associate Laboratory i4HB—Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, 4050-313 Porto, Portugal
[6]Faculty of Pharmacy, University of Coimbra, 3004-531 Coimbra, Portugal
[7]Center for Neuroscience and Cell Biology, 3004-504 Coimbra, Portugal
**esousa@ff.up.pt*

The most common cutaneous symptom, pruritus, is an innate response to protect the skin against irritants. When it lasts more than six weeks, it is considered chronic pruritus (CP) having a high negative impact on quality of life. This symptom is present mainly in inflammatory dermatological conditions existing an unmet need for effective treatments since the current therapy lacks effectiveness [1]. The pathophysiology is not fully elucidated being associated with various mediators and receptors, namely neurokinin 1 receptor (NK1R) and its agonist substance P. The development of new therapeutic strategies based on NK1R as a target appears to be a promising strategy due to the recent disclosure of its crystallographic structure [2]. Fiscalins are associated with a wide range of activities and can be considered as privileged structures with a high potential to furnish drug candidates [3]. Therefore, aiming to find a new therapeutic strategy for CP, a library of fiscalins, inspired by the marine-derived and NK1R antagonist fiscalin B, was tested *in silico* for its binding affinity to NK1R, and *in vitro* regarding cytotoxicity and anti-inflammatory activities.

Promising results were obtained in docking studies, since a higher binding affinity for the tested fiscalins was obtained when compared to fiscalin B, previously described as substance P antagonist. The safety profile of the fiscalins was assessed in macrophages, and no relevant cytotoxicity was observed for most of the in-house library of compounds. Furthermore, their potential anti-inflammatory activity was addressed using an *in vitro* macrophage based model of inflammation and encouraging results were obtained, since the production of the pro-inflammatory mediator oxide nitric was reduced in 50% for some of the tested compounds even at the smaller tested concentration (12.5 µM). A preliminary structure-activity relationship could be proposed.

Overall, the achieved results demonstrated that fiscalins are potentially a new source of substance P antagonists and, considering the *in silico* studies as well, they appear to be promising candidates for discovery of an efficient treatment of CP. In the future, the cytotoxicity on keratinocytes will also be accessed, together with the underlying molecular pathways responsible for the anti-inflammatory activity.

Aknowledgments

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Beyond chemical bonds

Cláudia Nunes[1,2,*], Salette Reis[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade Do Porto, Porto, Portugal
[2]ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Porto, Portugal
**cdnunes@ff.up.pt*

Chemical bonds drive the outcome of most reactions. In my research, they led to the development of new nanoplatforms and also explain the interaction between them and bioactive molecules. In the path of these discoveries, besides the very important chemical bonds, social ones were decisive for the flow of the research. In this communication, I will highlight some works that were developed together with Professor José L.F. Costa Lima and how these bonds contributed to the advance of the work, stimulating to think differently.

- The study of the influence of ten phenolic compounds, considered by E.P.A. (Environmental Protection Agency) as priority pollutants (phenol; 2-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; pentachlorophenol; 2,4-dimethylphenol; 2-nitrophenol; 2,4-dinitrophenol; 2-methyl-4,6-dinitrophenol) in the fluidity of the cellular membrane. Studies have been effectuated in biological systems, for which the kind of chosen cells were mice splenocytes, and in artificial systems - liposomes. All studied phenolic compounds were able to increase the fluidity of the cells and the liposome membranes [1].
- Notwithstanding the similar chemical structures of nonsteroidal anti-inflammatory drugs (NSAIDs), these drugs have a different biological impact, concerning their therapeutic and side effects. The NSAIDs studied were chosen because of their common use in therapeutics and their structural, chemical and functional diversity. In order to identify and isolate the effect of different membrane parameters on the interaction of these drugs; membrane mimetic models (micelles, liposomes, monolayers and supported lipid bilayers) were used, once these models show structural similarities to the lipid matrix of biomembranes. Essentially three types of studies were carried out: membrane partitioning, membrane location and biophysical modifications of the membrane [2,3].
- Albeit DNA has held the center stage as primary target, the mechanisms of action of anthracyclines are still a matter of considerable debate. The plasma membrane is the initial encountered barrier and a primary action on the physicochemical properties of the cell membrane could trigger a series of events responsible for their cytotoxic action. Thus, we investigated the interaction of anthracyclines with lipid membranes and their ability to bind to surface-active phospholipids, as well as their effect on the lipid dynamic properties of membrane models, once the results may help to further understand their mode of action [4,5].

Acknowledgements

To the deep impact that Professor José L.F. Costa Lima had in our research group.

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Bladder Cancer: The Future of Diagnostic and Patient Monitoring

Rafael Bento[1,2,*], Luís B. Carvalho[1,2], Inês Domingos[1,2], Carlos Lodeiro[1,2], Luis Campos Pinheiro[3,4], Hugo Santos[1,2,5], José-Luis Capelo-Martínez[1,2,ϕ]

[1]BIOSCOPE Research Group, LAQV-REQUIMTE, Department of Chemistry, Faculty of Science and Technology, Univesidade NOVA de Lisboa, 2829-516, Campus de Caparica, Portugal; [2]PROTEOMASS Scientific Society, Madan Parque, Rua dos Inventores, 2825-182, Caparica, Portugal;
[3]Serviço de Urologia, Centro Hospitalar de Lisboa Central, Lisboa, Portugal;
[4]Faculdade de Ciências Médicas, Universidade NOVA de Lisboa, Lisboa, Portugal;
[5]Department of Pathology, University of Pittsburgh Medical Center, Pittsburgh, PA, United States.
*rg.bento@campus.fct.unl.pt | ϕ jlcm@fct.unl.pt

Background: The use of biomarkers as a diagnostic and prognostic tool for diseases has revealed many shortcomings, with the vast majority of these having very limited diagnostic and prognostic value. A lot of the newly discovered biomarkers are not directly tied to the disease itself, but stem instead from physiological conditions brought on by the disease, which reduces their prognostic value, or even treatment response evaluation. Furthermore, patient phenotype is another major shortcoming, and the role it plays in biomarker response. However, modern mass spectrometry has opened up a world of new possibilities to use the evolution of the patient's proteome to evaluate the disease progression. High resolution mass spectrometry allows for the monitoring of the levels of thousands of proteins, instead of just the few biomarkers, and can provide insight into the roles proteins play in the biochemical pathways they are involved in. Thus, it becomes easy to evaluate which biochemical pathways the disease is affecting, as well as to evaluate the treatment response providing thus useful insight into therapy adjustment.

Objectives: Updating the Medical community on the latest trends in Personalised Medicine based proteomics thought the study of bladder cancer patients.

Methods: The proteome of seventeen T1 stage bladder cancer patients were deep mining and compared using bioinformatics to unveil prognostic.

Results: Prognostic is possible based on the patient´s levels of hallmarks of cancer.

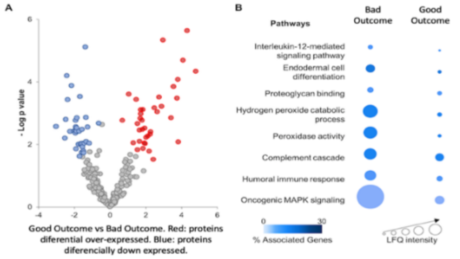

Figure 1. A. Volcano plot of proteins identified in both groups of patients. **B.** Pathway legend.

Conclusions: Overall, the proteomic analysis revealed a large number of biochemical pathways dysregulated at a different level for patients with poor or bad outcome.

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QS70

Development of a Robust Ultrasonic-Based Sample Treatment to Unravel the Proteome of OCT-Embedded Solid Tumor Biopsies

Pedro Campos[1,2,*], Susana Jorge[1,2], José L. Capelo[1,2], William LaFramboise[3], Rajiv Dhir[3], Hugo M. Santos[1,2,ϕ], Carlos Lodeiro[1,2]

[1]BIOSCOPE Research Group, LAQV-REQUIMTE, Department of Chemistry, Faculty of Science and Technology, Univesidade NOVA de Lisboa, 2829-516, Campus de Caparica, Portugal; [2]PROTEOMASS Scientific Society, Madan Parque, Rua dos Inventores, 2825-182, Caparica, Portugal; [3]Department of Pathology, University of Pittsburgh Medical Center, Pittsburgh, Pennsylvania 15261, United States.

*pad.campos@campus.fct.unl.pt | ϕ hmsantos@me.com

Background: The issues caused by polymers present in optimum cutting temperature (OCT)-embedded tissue in its preparation for mass spectrometry analysis are promised to be resolved by a helpful three-step proteomics workflow. It starts by the cleaning of the OCT-embedded tissue biopsies making use of ethanol and water in a sequential series of ultrasonic washes in an ultrasound bath. Subsequently a quick ultrasonic-assisted extraction of proteins is performed by an ultrasonic probe. Finally, a rapid ultrasonic digestion of complex proteomes is done using a microplate horn assembly device. In order to demonstrate its feasibility, the workflow was applied to human normal and tumour kidney biopsies including chromophobe renal cell carcinomas (chRCCs) and renal oncocytomas (ROs). Applying this new approach high sample throughput and good proteome recovery is achieved from OCT samples.

Objectives: Overcome the pitfalls caused by polymers present in optimum cutting temperature (OCT) embedded tissue during its preparation for mass spectrometry analysis.

Results: Ultrasonic energy can be used in the cleaning of samples, in accelerating the digestion of complex proteomes, and in reducing the time and handling necessary in tedious proteomics workflows. Furthermore, it can be scaled up for use in high-throughput applications.

Conclusions: A new ultrasonic-based proteomics workflow for analysis of OCT-Embedded tissues and biopsies was developed. Additionally, this proof-of-concept study hints that this new proteomic workflow has the capability to discriminate between chromophobe renal cell carcinoma from renal oncocytoma.

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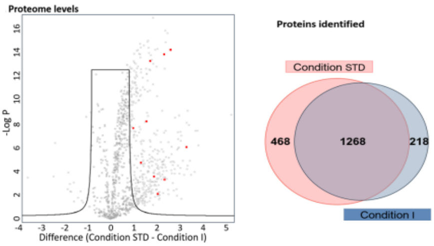

Figure 1. A. Volcano plot representation of the differentially expressed proteomes between condition I (ultrasonic method) and condition STD. **B.** Venn diagram representing the number of overlapped proteins identified between condition I and condition STD.

Biotin-bearing squaraine dyes as potential antitumor photodynamic agents: an *in vitro* preliminar study

Eurico Lima[1,2*], Octávio Ferreira[2], Renato Boto[2], José R. Fernandes[1], Paulo Almeida[2], Samuel M. Silvestre[2,3], Adriana O. Santos[2], Lucinda V. Reis[1]

[1]Chemistry Centre of Vila Real (CQVR), University of Tras-os-Montes and Alto Douro,
Quinta de Prados 5001-801, Vila Real, Portugal
[2]Health Sciences Research Centre (CICS-UBI), University of Beira Interior,
Av. Infante D. Henrique 6201-506, Covilhã, Portugal
[3]Centre for Neuroscience and Cell Biology (CNC), University of Coimbra,
Rua Larga 3000-517, Coimbra, Portugal
**eurico_lima@icloud.com*

The combination of potential anticancer molecules with biomolecules is reported in the literature as a way to significantly improve their targeting and specificity, one of the most critical issues in the modern pharmaceutical industry [1]. For example, biotin, also known as vitamin B7 or coenzyme-R, is a biomolecule consisting of a ureido ring fusing with a tetrahydrothiophene ring, whose relevance is correlated with the fact that there are overexpressed receptors in numerous tumor cell lines, namely of ovarian origin, lung, breast, among others [2]. Several compounds have been conjugated with this biomolecule, and the results have been quite appealing: curcumins [3] as chemotherapeutic agents and chlorins [4] as photosensitizing agents are some examples.

This communication presens the methods of synthesis of *N*-ethyl and *N*-hexyl-chain benz[*e*]indole-based biotin-bearing squaraine dyes, as well as their photophysical and photochemical properties such as light stability and singlet oxygen formation ability. A preliminary approach to their photodynamic activity is presented, showing their cell viability biological effects under irradiated and non-irradiated conditions against the Caco-2 and HeLa tumor cell lines, reported in the literature as cells with a great biotin uptake level and high biotin-receptor expression, respectively [2,5].

Both squaraine dyes exhibited photophysical properties indicative of their promised phototherapeutic application, such as a worthy absorption capacity in the red region (~ 700 nm) but low to moderate singlet oxygen production ability. The results of the biological assays show statistical differences in the toxicity of the dye between the irradiated and non-irradiated conditions more extensively for colorectal cancer cells. For the HeLa cell line, the photodynamic effects were not so evident. In the near future, in addition to desiring to evaluate these dyes in normal cell lines to understand whether the biotin introduction into the squaraine-core molecular structure resulted in a selective effect, the authors intend to understand whether effects variance between cell lines are due to a protective effect on cells or to a differentiated dyes' uptake by different cell lines.

Acknowledgments

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How the selectivity of Zn(II) ligands towards G4 DNA structures is influenced by the number and position of the positive charges

Catarina I. V. Ramos[*], **Nuno M. M. Moura, Leandro M. O. Lourenço, M. Graça P. M. S. Neves**

LAQV-REQUIMTE, Department of Chemistry of University of Aveiro, 3810-193 Aveiro, Portugal
[*]*c.ramos@ua.pt*

Telomerase is a reverse transcriptase enzyme over-expressed in almost 90% of human cancers, thus being highly used as target for the development of new anticancer drugs. Other important targets are oncogenes and tumour suppressor genes due to their strict correlation with the initiation and progression of tumours [1]. Considering that G-quadruplex (G4) oligonucleotides are present in most human telomeres and oncogene promoters, the development of molecules with ability to stabilize these DNA structures is being considered a promising strategy in modern research aiming to find new potential anticancer drugs. This approach can contribute to downregulate transcription or to block telomere elongation in cancer cells, by stalling the DNA replication machinery tool and consequently, to block telomerase activity.

Using biophysical and biochemical methods, the ability of several families of ligands for telomerase inhibition and regulation of genes expression, by adduct formation with G-quadruplexes is being evaluated with promising results (figure 1) [2-7]. Under this context, porphyrins and phthalocyanines have been pointed out as promising G4 stabilizing ligands [3-7].

Following our interest in this field [2-7], we report here the ability of Zn(II) complexes of two porphyrins both bearing four positive charges and also of two phthalocyanines, one owning four and the other eight positive charges in the stabilization of G4 structures. Within the series of studied compounds, it was found that a higher number of charges resulted in a positive effect on the interaction, although a balance between the number of charges and their position seems to be essential for better stabilization. Data obtained showing that all the studied molecules present high affinity to G4 structures, with different selectivity, depending on the structure of the ligands, will be pointed out and discussed.

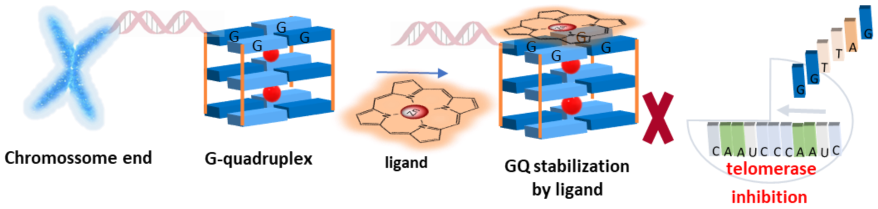

Fig. 1. G-quadruplex DNA stabilization by ligands and telomerase inhibition.

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Low serum bromine levels in chronic hemodialysis patients – is there any clinical impact?

Mary Duro[1,2,3*], Gergana Novakova[3,4], Presian Bonev[3,4], Rui Azevedo[3], Cristina Couto[3,5], Edgar Pinto[3,6], Agostinho Almeida[3]

[1]FP-ENAS – Fernando Pessoa Energy, Environment and Health Research Unit, Universidade Fernando Pessoa, Praça de 9 de Abril 349, 4249-004 Porto, Portugal.
[2]Laboratório de Análises Clínicas Dra. Matilde Sampaio, Lda., Reta de Vale da Madre 3, 5200-216 Mogadouro, Portugal & Laboratório de Análises Clínicas Vale do Sousa, Av. José Júlio 281, 4560-547 Penafiel, Portugal.
[3]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4]Medical University - Varna, Marin Drinov 55, 9002 Varna, Bulgaria.
[5]TOXRUN – Toxicology Research Unit, Instituto Universitário de Ciências da Saúde (IUCS), CESPU, Av. Central de Gandra 1317, 4585-116 Gandra PRD, Portugal.
[6]Department of Environmental Health, School of Health, P.Porto, Rua Dr. António Bernardino de Almeida 400, 4200-072 Porto, Portugal.
*mcduro@gmail.com, mduro@ufp.edu.pt

Background: Patients on chronic hemodialysis therapy are at high risk for disturbed trace element status due to both the underlying disease and the hemodialysis process itself [1]. Data on serum bromine levels in these patients are scarce.

Methods: Using an ICP-MS analytical procedure, serum bromine levels were determined in a cohort of end-stage renal disease patients on chronic hemodialysis (n=57; 68.9±14.0 years old; male/female ratio: 1.37). The results were compared with those of a control group (individuals without evidence of kidney disease according to standard clinical laboratory criteria who attended the same clinical laboratory for routine analyses: n=59; 57.4±17.9 years old; male/female ratio: 0.90).

Results: Hemodialysis patients had much lower serum bromine levels than controls: **1086**±244 vs. **4137**±770 µg/L; P<0.0001.

Discussion: Bromine (bromide in plasma) showed to be extensively removed from plasma due to the hemodialysis process. The actual impact of this bromine "deficiency" is unknown. Bromine has not generally been considered an "essential" element [2], however, evidence of possible essentiality has been growing [3].

In particular, bromine has been linked to brain metabolism: it is used as a sedative to induce sleep, increases in animals during hibernation as well as in sleeping humans; and a bromine compound with REM sleep-inducing and anti-choline esterase activities (1-methylheptyl gamma-bromoacetoacetate) was identified in human cerebrospinal fluid [4].

On the other hand, estimates suggest that 40-85% of hemodialysis patients have sleep disorders, mainly insomnia [5]. Thus, the possibility has been raised that the bromine "deficiency" found in these patients may be associated with sleep the disorders that affect them.

This is an interesting hypothesis that requires further clinical investigation.

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Trace element imbalances in hemodialysis patients: new data from a cohort of Portuguese patients

Mary Duro[1,2,3*], Rui Azevedo[3], Félix Costa[3,4], Edgar Pinto[5], Agostinho Almeida[3]

[1]FP-ENAS – Fernando Pessoa Energy, Environment and Health Research Unit, Universidade Fernando Pessoa, Praça de 9 de Abril 349, 4249-004 Porto, Portugal.
[2]Laboratório de Análises Clínicas Dra. Matilde Sampaio, Lda., Reta de Vale da Madre 3, 5200-216 Mogadouro, Portugal & Laboratório de Análises Clínicas Vale do Sousa, Av. José Júlio 281, 4560-547 Penafiel, Portugal.
[3]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[4]Hospital Militar Principal/Instituto Superior, Rua Nicolau Gomes Spencer, Luanda, Angola.
[5]Department of Environmental Health, School of Health, P.Porto, Rua Dr. António Bernardino de Almeida 400, 4200-072 Porto, Portugal.
mcduro@gmail.com; mduro@ufp.edu.pt

Patients with end-stage renal disease undergoing hemodialysis (HD) therapy are at risk of developing deficiencies of essential trace elements and/or overload of toxic trace elements, both of which may significantly affect their clinical status. Those imbalances may result from the disease itself but also from the therapy, namely the hemodialysis process.

This work aimed at evaluate the current trace elements status in a cohort of patients under hemodialysis therapy. Serum (n=88) and whole blood samples (n=108) from HD patients, collected during the routine periodic control of Al levels, were analyzed for a wide panel of trace elements using inductively coupled plasma mass spectrometry (ICP-MS) (HD group). For comparison purposes, both serum (n=16) and whole blood samples (n=59) of individuals attending the same Clinical Laboratory but with no evidence of renal disease according to standard laboratory analytical criteria were also analysed (Control group).

The results showed significant differences among the hemodialysis patients group and the control group for several trace elements (Table 1):

Table 1. Trace element levels [µg/L; mean (sd)] in HD patients and control group

	SERUM		**WHOLE BLOOD**	
Element	**HD patients** (n=88)	Controls (n=16)	**HD patients** (n=108)	Controls (n=59)
Li	**2.9 (1.8)**	1.2 (0.8)	**2.7 (1.9)**	1.1 (0.8)
B	**89 (43)**	34 (17)	**133 (62)**	46 (23)
Mn	*0.40 (0.10)*	0.52 (0.11)	8.4 (2.3)	7.6 (1.5)
Co	**0.23 (0.11)**	0.13 (0.04)	*0.19 (0.06)*	0.23 (0.05)
Ni	**2.80 (0.95)**	1.09 (0.25)	**1.82 (0.46)**	1.53 (0.69)
Cu	*670 (151)*	812 (139)	*844 (138)*	955 (167)
Zn	*450 (86)*	681 (115)	5345 (766)	5767 (2249)
Se	*62 (13)*	82 (15)	*123 (20)*	138 (20)
Rb	*87 (23)*	115 (19)	*1145 (230)*	3510 (958)
Sr	**29.0 (3.7)**	22.3 (7.6)	**29.9 (4.0)**	17.6 (6.7)
Mo	**3.7 (1.5)**	1.11 (0.42)	**3.2 (1.6)**	0.81 (0.28)
Cd	**0.04 (0.02)**	0.01 (0.01)	**1.00 (0.32)**	0.24 (0.11)
Pb	**0.29 (0.15)**	0.10 (0.08)	**100 (24)**	21 (14)

[a] Results in bold are significantly ($p<0.001$) higher than in the control group. Results in italics are significantly lower.

This work provides further evidence on imbalances in trace element levels in hemodialysis patients. The results obtained for serum are generally in agreement with those found in previous studies [1]. Results obtained for whole blood samples (which are much scarcer in the literature) globally showed the same trend, except for Mn.

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Association between natural exposure to lithium and suicide rate: an ecological and human biomonitoring study in northern Portugal

Agostinho Almeida[1*], Carolina Gonçalves[2], Rui Azevedo[1], Félix Costa[1,3], Cristina Couto[1,4], Mary Duro[1,5,6], Agostinho Santos[1,2,7,8], Laura Cainé[1,2,7]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[2]FMUP – Faculdade de Medicina da Universidade do Porto, Alameda Prof. Hernâni Monteiro, 4200-319 Porto, Portugal.
[3]Hospital Militar Principal/Instituto Superior, Rua Nicolau Gomes Spencer, Luanda, Angola.
[4]TOXRUN – Toxicology Research Unit, Instituto Universitário de Ciências da Saúde (IUCS), CESPU, Av. Central de Gandra 1317, 4585-116 Gandra PRD, Portugal.
[5]FP-ENAS – Fernando Pessoa Energy, Environment and Health Research Unit, Universidade Fernando Pessoa, Praça de 9 de Abril 349, 4249-004 Porto, Portugal.
[6]Laboratório de Análises Clínicas Dra. Matilde Sampaio, Lda., Reta de Vale da Madre 3, 5200-216 Mogadouro, Portugal & Laboratório de Análises Clínicas Vale do Sousa, Av. José Júlio 281, 4560-547 Penafiel, Portugal.
[7]INMLCF – Instituto Nacional de Medicina Legal e Ciências Forenses, Jardim Carrilho Videira, 4050-167 Porto, Portugal.
[8]Escola de Medicina da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
aalmeida@ff.up.pt

Several studies have found an inverse relationship between lithium levels in drinking water and the suicide rate in the general population [1,2]. However, this observation has failed in other studies [3], including in Portugal [4], and there seems to be a threshold concentration (30 µg/L) above which this "protective" effect of lithium becomes noticeable [3].

The main limitation of these "ecological" studies is that they assume a direct association between lithium concentration in drinking water and population lithium intake. However, other sources can significantly contribute to the total daily intake of lithium, namely various dietary sources.

Determination of urinary lithium levels may be a better approach in the study of this issue (the possible association between natural lithium exposure and suicide rates), by allowing a more accurate assessment of actual lithium intake by the general population.

In this context, we conducted a comparative study between two regions of northern Portugal with very different relative risk (RR) for suicide, according to a study by Loureiro et al. [5], roughly corresponding to the metropolitan area of Porto ("AMP"; west/coast, with the lowest RR nationally: 0.28) and the region of Trás-os-Montes ("TM"; northeast, with the third highest RR: 1.67). The study included both the determination of lithium concentration in water samples (from domestic public supply and other sources, including surface water) and in urine samples from individuals residing in the two regions.

There was no clear inverse association between lithium levels and the RR of suicide. The *median* concentration in **water** was slightly higher in the region with the lowest RR (AMP) [3.4 µg/L (n=59) vs. 2.5 µg/L (n=72)], but the *median* concentration in **urine** was lower [22.6 µg/L (n=131) vs. 27.5 µg/L (n=51)]. However, in this region (AMP) a significantly higher percentage of individuals with high lithium urinary levels (> 80 µg/L) was found: 15% (20/131) vs. only 6% (3/51). The reasons for this large inter-individual variability in urinary lithium levels should be investigated.

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Reference intervals for whole blood trace elements in the Angolan adult population

Félix Costa[1,2*], **Mariquinha Carvalho**[2], **Rui Azevedo**[1], **Gonçalo Ferreira**[1], **Inês Gonçalves**[1], **Beatriz Sousa**[3], **Cláudio Sousa**[4], **Elisa Francisco**[2], **Delfina Kipanda**[2], **Mary Duro**[1,5], **Agostinho Almeida**[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[2]Hospital Militar Principal/Instituto Superior, Rua Nicolau Gomes Spencer, Luanda, Angola.
[3]Hospital Municipal de Talatona, Rua do ENAPP, Luanda, Angola.
[4]Direcção dos Serviços de Saúde do EMG/FAA, Largo dos Ministérios, Luanda, Angola.
[5]FP-ENAS – Fernando Pessoa Energy, Environment and Health Research Unit, Universidade Fernando Pessoa, Praça de 9 de Abril 349, 4249-004 Porto, Portugal.
felix.costa.hmp@gmail.com

Well-established reference intervals (RIs) are essential for the correct interpretation of individual patient laboratory results. According to current guidelines, laboratory specific RIs should be established, which take into account the analytical methodology used and the characteristics of the population covered [1].

In a previous work, we defined reference intervals for trace elements in the serum of the Angolan adult male population [2]. The objective of the present work was to establish RIs for whole blood trace elements in the Angolan adult population.

Whole blood samples were collected from blood donors who attended the Hospital Militar Principal/IS, Luanda, Angola, from 09.2021 to 03.2022. A total of 150 apparently healthy subjects (81% male) were included in the study. The mean age was 32±6 (range 19–50) years. Samples were collected into BD Vacutainer® Trace Element K2 EDTA (K2E) tubes. Trace element analysis was performed by inductively coupled plasma mass spectrometry (ICP-MS; Thermo iCAP™ Q instrument) using a validated analytical procedure, under strict analytical quality control (Seronorm™ Trace Elements Whole Blood, L-1, L-2 and L-3). RIs were calculated according to the Clinical Laboratory Standards Institute (CLSI) EP28-A3c guideline [3]. Tukey's method was used to detect outliers. The Kolmogorov-Smirnov test was used to verify the normality of the data distribution. Statistically significant differences between male and female whole blood trace element levels were assessed using t-student or Mann-Whitney tests, depending on the normal or non-normal variables data distribution, respectively.

There were no statistically significant differences between male and female trace element concentrations ($p > 0.05$). The 95% RI (µg/L) obtained were as follows:

a) *essential trace elements* - Mn: 4.7-11.7; Co: 0.31-0.53; Cu: 647-1039; Zn: 3594-7676; Se: 115-244; Mo: 0.25-2.00;
b) *non-essential/toxic trace elements* - Li: 0.34-1.76; Be: < 0.01; Ni: 2.3-4.0; As: < 6.9; Rb: 1821-3587; Sr: 14.2-39.2; Cd: < 0.67; Cs: 1.03-2.54; Ba: 0.28-1.43; Hg: 1.29-8.14; Tl: < 0.08; Pb: 21.8-105.9.

RIs have been stablished for a wide panel of trace elements in whole blood of the Angolan adult population, thus providing an important tool for future research studies and for the clinical and toxicological laboratory evaluation of individual patients.

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The effect of repeated blood donation on whole blood trace element status – a cross-sectional study in Angolan donors

Rui Azevedo[1*], **Félix Costa**[1,2], **Mariquinha Carvalho**[2], **Gonçalo Ferreira**[1], **Inês Gonçalves**[1], **Beatriz Sousa**[3], **Cláudio Sousa**[4], **Elisa Francisco**[2], **Delfina Kipanda**[2], **Mary Duro**[1,5], **Agostinho Almeida**[1]

[1]LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal.
[2]Hospital Militar Principal/Instituto Superior, Rua Nicolau Gomes Spencer, Luanda, Angola.
[3]Hospital Municipal de Talatona, Rua do ENAPP, Luanda, Angola.
[4]Direcção dos Serviços de Saúde do EMG/FAA, Largo dos Ministérios, Luanda, Angola.
[5]FP-ENAS – Fernando Pessoa Energy, Environment and Health Research Unit, Universidade Fernando Pessoa, Praça de 9 de Abril 349, 4249-004 Porto, Portugal.
**ruiazevedo43@gmail.com*

Except for iron, there is a great paucity of data on the effect of repeated blood donation on trace elements status [1]. In a previous work, we studied the effect of repeated blood donations in *serum* trace element levels on a sample of the Angolan adult population [2]. The aim of this study was to assess the effect of repeated blood donation on *whole blood* trace element levels.

Samples were collected from blood donors who attended the Hospital Militar Principal/IS, Luanda, Angola, from 09.2021 to 03.2022. A total of 150 apparently healthy subjects (81% male) were included in the study. The mean age was 32±6 (range 19–50) years. Samples were collected into BD Vacutainer® Trace Element K2 EDTA (K2E) tubes.

Every participant completed a written questionnaire with socio-demographic data and blood donation history. Trace element determination (Li, Be, Mn, Co, Ni, Cu, Zn, Se, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, Tl, Pb) was performed by inductively coupled plasma mass spectrometry (ICP-MS; Thermo iCAP™ Q instrument) using a validated analytical procedure, under strict analytical quality control (Seronorm™ Trace Elements Whole Blood, L-1, L-2 and L-3).

Statistical analysis was performed with SPSS Version 27.0 statistic software package. Tukey's method was used to detect and remove outliers. Kolgomorov-Smirnov and Shapiro-Wilk tests were used to assess data distribution normality. Statistically significant differences between male and female trace element levels were assessed using t-student test for normally distributed variables or Mann-Whitney test for non-normally distributed variables. Statistically significant differences in trace element levels according to the number of previous blood donations were assessed with Kruskall-Wallis test with Bonferroni multiple tests correction for variables with non-normal distribution. For normally distributed variables, Welch test (in case of inhomogeneity of variance) or One Way Analysis of Variance (ANOVA) with Games-Howell multiple tests correction was used.

There was no statistically significant difference between male and female trace element concentrations ($p>0.05$). According to the answers to the written questionnaire, subjects were divided into 3 groups: group I: first time donors; group II: 1-2 blood donations in the last 3 years; group III: ≥3 blood donations in the last 3 years. No statistically significant differences were observed between the three groups except for **Rb** [group I *vs.* group II (2833±568 *vs.* 2585±426; $p=0.049$) and group II *vs.* group III (2585±426 *vs.* 2842±423; $p=0.014$) and for **Cs** [group II *vs.* group III (1.57±0.05 *vs.* 1.82±0.06; $p=0.011$)].

Repeated blood donation does not appear to significantly affect the status of trace elements in the blood of donors, namely the levels of essential trace elements.

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Synthesis of new purine nucleosides as potential biometal chelators and cholinesterase inhibitors

Catarina Maria[1,2*], João M. Barros[1], Nuno M. Xavier[1], Karina Shimizu[1], Adilson A. Freitas[1], Maria J. Ferreira[1], Ignazio Schino[3], Mariangela Cantore[3], Modesto de Candia[3], Nicola Colabufo[3], José N. C. Lopes[1], Amélia P. Rauter[1]

[1]Centro de Química Estrutural, Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal, and Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
[2]NOVA School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal
[3]Università degli Studi di Bari, Dipartimento di Farmacia-Science del Fármaco, 70121 Bari, Italy
**c.maria@campus.fct.unl.pt*

Alzheimer's disease (AD) is a neurodegenerative pathology that is caused by multiple factors, including the progressive decline of the level of acetylcholine, an important neurotransmitter [1], and the deregulation of biometals homeostasis, such as copper, iron and zinc [2].

Acetylcholine may be hydrolyzed by two enzymes, acetylcholinesterase and butyrylcholinesterase [3], and the current therapeutic strategies are mainly based on treating AD patients with these enzyme inhibitors. Although these strategies are focused on disease symptomatic relief, recent studies have shown that the long-term use of these compounds may actually lead to disease modifying benefits [4].

The deregulation of the biometals homeostasis is related to oxidative stress and to the induction of Ab aggregation and of tau hyperphosphorylation, two main characteristics of the disease [2].

Thus, the discovery of multitarget drugs is an interesting challenge towards finding a disease modifying therapy. In this context, mannosylpurines synthesized in our group already showed potent and selective butyrylcholinesterase inhibition [5]. Aiming at discovering such multitarget drug candidates, a new series of mannosyl and rhamnosylpurines was synthesized and their properties as biometal chelators and cholinesterase inhibitors were evaluated. The results obtained will be presented and discussed.

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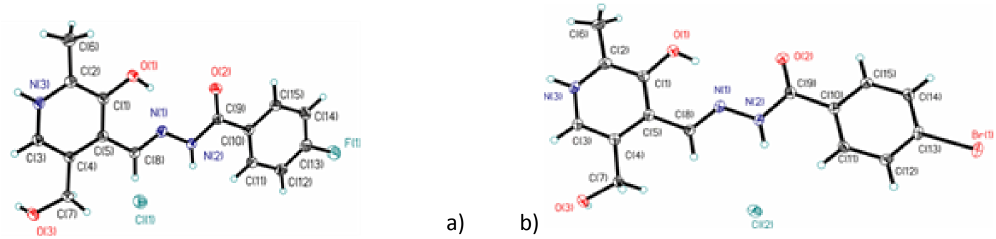
New halogen hydrazones derived from pyridoxal and their biological behavior

Fernando Avecilla[1], Antía Sar-Rañó[1], Lucía Mato-López[1], Lucía Ramos-Pan[1], Iago Vázquez-Ansemil[1], Miguel Maestro[1], Josefina Méndez[1], Vanessa Valdiglesias[1], Natalia Fernández-Bertólez[1]

[1]Universidade da Coruña. Grupo NanoToxGen, Centro de Investigacións Científicas Avanzadas, As Carballeiras, s/n, San Vicenzo de Elviña 15008, A Coruña, España.
fernando.avecilla@udc.es

Halogen hydrazones derived from pyridoxal were synthetized in methanol solution and characterized by NMR, MS, IR and single crystal X-ray diffraction. Compounds **1** and **2** are substituted with fluorine in *meta* and *para* positions and compounds **3** and **4** are with bromide in *meta* and *para*, respectively. Fig.1 shows the structures obtained for some of these compounds. UV-Visible study of the interaction with DNA was carried out and the binding constant were determined using Benesi-Hildebrand[1], $K_b = 3.3604 \cdot 10^4$ and Wolfe-Shimer [2], $K_b = 3.3484 \cdot 10^4$, equations (see an example in Fig.2)



a) b)

Fig.1. ORTEP of the crystal structure in *p*-halogen hydrazone compounds **2**(a) and **4**(b).

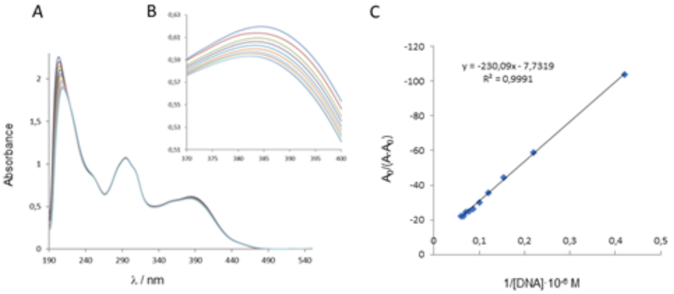


Fig.2. (A) Absorption spectra of the *m*-bromine hydrazone, compound **3,** in 0.1 M phosphate buffer (pH 7.2) containing 10% ethanol in the presence of increasing amounts of DNA. (B) Widening of the absorption band at 380-390 nm. (C) Plots of $A_0/(A-A_0)$ *vs.* 1/[DNA] for the determination of binding constant of compound **3**-DNA adducts, according to Benesi-Hildebrand equation [1].

The cytotoxicity of these compounds was tested on human hepatocarcinoma A549 cellular line. After 48 h treatment, IC_{50} values for the **1** and **3** compounds were 257.86 ± 60.54 µM and 18.17 ± 7.51 µM, respectively.

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Benz[*e*]indole and indolenine squaraine dyes derivatives as antifungal agents and fluorescent probes

Lucinda V. Reis[1*], Vanessa S. D. Gomes[1,2], João C. C. Ferreira[2,3,4], Renato E. Boto[5], Paulo Almeida[5], Jose R. Fernandes[6], Maria João Sousa[3,4], M. S. T. Gonçalves[2]

[1]Centre of Chemistry -Vila Real (CQ-VR) / Department of Chemistry, University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal
[2]Centre of Chemistry (CQ-UM) / Department of Chemistry, University of Minho,
Campus of Gualtar, 4710-057 Braga, Portugal
[3]Centre of Molecular and Environmental Biology (CBMA) / Department of Biology, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal
[4]Institute of Science and Innovation for Bio-Sustainability (IBS), University of Minho,
Campus of Gualtar, 4710-057 Braga, Portugal
[5]Health Sciences Research Centre (CICS-UBI) / Department of Chemistry, University of Beira Interior, Av. Infante D. Henrique, 6201-506 Covilhã, Portugal
[6]Physical Department, University of Trás-os-Montes and Alto Douro,
Quinta de Prados, 5001-801, Vila Real, Portugal
**lucinda.reis@utad.pt*

Since the first reports in the history of humanity, society has suffered from various diseases of infectious origin constituting one of the main causes of mortality. Currently, fungal infections continue to be an emerging problem that has increased exponentially in recent decades, and is still responsible for over one-third of deaths worldwide [1]. A healthy individual is able to cohabitate with disease-causing fungal agents, but when there is a breakdown of the immune system or high exposure to these agents, an infectious disease is triggered that can be asymptomatic or can rapidly progress to a lethal systemic disease [2-4]. The successful treatment of these diseases is essentially based on rapid diagnosis and the application of an antifungal agent that acts quickly and effectively.

In this work we present the antifungal performance of some squaraine dyes derived from benzo[*e*]indole and indolenine, as well as the possible use as fluorescent probes for detection and quantification of human serum albumine (HSA).

Regarding the antifungal activity, this was studied through a broth microdilution assay using *Saccharomyces cerevisiae* PYCC 4072 as a biological model. The effect of irradiation of the dyes, with an appropriate light emitting diode system, on the antifungal activity was also evaluated, and it was verified that some of the dyes improve their activity after irradiation. Using fluorescence microscopy techniques, the colocalization of dyes in *S. cerevisae* cells was investigated and it was possible to verify that some of the squaraine dyes with a barbituric moiety in the four-membered central ring stained and accumulated preferentially in the mitochondrial web and perinuclear membrane of the cells. The possible use as fluorescent probes for the detection of HSA was also evaluated, demonstrating a linear variation of the fluorescence intensity accompanied by the increase of the HSA protein concentration.

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Exploring the bioactive potential of *Artemisia annua* L. hydroethanolic extracts obtained by microwave-assisted extraction

Mohamed Amine Mahjoub[1,2], Ricardo C. Calhelha[1,2], Maria José Alves [1,2], Lillian Barros[1,2], Simão Pinho[1,2] Manuel Ayuso[1,2*]

1 Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
2 Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
**Corresponding author: m.ayuso@ipb.pt*

Artemisia annua L. is known for producing artemisinin, a sesquiterpene lactone compound, which is applied to treat of malaria [1]. Its pharmacodynamic and pharmacokinetic characteristics, as well as its strong capacity for *Plasmodium* elimination, have raised many expectations for this new class of antimalarial drugs [2]. However, this plant has been also used in traditional Chinese medicine to treat of various diseases since ancient times. Recent studies have focused on its extensive biological activities, which makes this plant an excellent candidate to be used in clinical therapies. Thus, this work aimed to evaluate different bioactivities from a hydroethanolic extract of *Artemisia annua*.

The plant extract in ethanol:water (80:20 v/v) was obtained by microwave-assisted extraction. The antioxidant activity was determined by thiobarbituric acid reactive substances (TBARS) assay, showing a potent activity with an IC_{50} of 10.3 ± 1.0 µg/mL. *A. annua* L. extract also exhibited antibacterial and antifungal properties, with concentrations ranging from 2.5 to 10 mg/mL. The ethanolic extract was very effective against the four tumor cell lines, presenting GI50 ranging from 21 to 61 µg/mL and excellent anti-inflammatory activity (38 µg/mL). However, it was also cytotoxic against the two normal cells tested (50 and 19 µg/mL).

Concluding, despite the excellent biological activities exhibited by *A. annua* L. extract, it was also demonstrated to be cytotoxic against normal cells. Therefore, further studies are necessary to study how the cytotoxicity of this extract could be reduced without affecting its bioactive properties.

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Development of a pH-sensitive dressing for clinical monitoring of chronic wounds

Ana B. Mesias, André D. Mayer, Renata M. Fernandes, Sara Baptista-Silva, Raquel B. R. Mesquita*, António O. S. S. Rangel

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005, Porto, Portugal
**rmesquita@ucp.pt*

Chronic wounds are a public health concern that require significant resources due to the frequent monitoring of their degree of infection, which implies a constant change of dressings.

The main objective of the project was to develop a qualitative pH indicator device capable of detecting pH variations in the bed of a chronic wound patient, through colorimetric changes. In this way, it is possible to know the infection status of the wound without removing the dressing. To obtain this analytical device, two different approaches were developed.

Firstly, a membrane made of polyvinyl chloride (PVC) was developed, with bromothymol blue (BTB) as pH indicator in a PIMAD (polymer inclusion membrane analytical device) approach [1]. This membrane showed a colour change from yellow to blue for pH values above 7.5, about 7.2 with no infection (Fig.1a) and above 7.5 infected chronic wound (Fig.1b). However, as BTB is irritating to the skin, this membrane had to be separated from the wound with a hydrophobic barrier, making it a complex membrane indicator. Then, a more natural and biocompatible option was explored and extracts from red cabbage (with a high content of anthocyanins) were used as pH indicator. The extract was obtained using boiling water, this way avoiding toxic organic solvents in an environmental friendly approach. Filter paper was embedded in the extract and incorporated into a transparent badge in a PAD (paper analytical device) approach. This approach enabled a highly visual colour change from purple (Fig.1 c) to blue (Fig.1 d) at the characteristic pH range for chronic wounds.

Both approaches were studied to attain the best (more visual and clear) pH change indication. In the end, the complexity of the assembly, the environmental sustainability and the economical aspect were taken into account for choosing the best approach, which proved to be the developed PAD. The simple implementation and visual the colour change enables to establish the degree of infection of the chronic wound, without having to remove the wound dressing, and to understand when to change the dressing, avoiding waste, reducing the inherent economic impact and improving patients' quality of life.

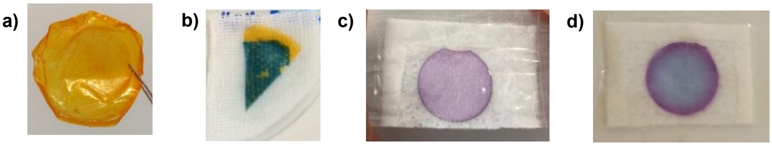

Fig.1. Developed indicator devices: PIMAD with BTB (a, b) and PAD with anthocyanins (c, d); simulation without infection (a, c) and with simulated infection (b, d).

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QUÍMICA TEÓRICA

Study of Sodium Hexanoate and Dodecanoate Salt-Based Eutectic Solvents by Molecular Dynamics Simulation Approach

Mariana H. Moreira[1], Isabel M. Marrucho[2], Luis C. Branco[3], Luís F. G. Martins[1,*]

[1]Universidade de Évora, Departamento de Química e Bioquímica, Évora, Portugal
[2]Universidade de Lisboa, Instituto Superior Técnico, Lisboa, Portugal
[3]Universidade Nova de Lisboa, REQUIMTE, Faculdade de Ciências e Tecnologia, Lisboa, Portugal
**lfgm@uevora.pt*

Hydrophobic deep eutectic solvent (DES) is a new type of green solvent, that has attracted the attention of researchers in recent years, however little is known about its structural conformation. The goal of the present study is to elucidate through molecular dynamics (MD) simulations, structural details and properties of DESs [1-5], obtained by the combinations of sodium hexanoate (NaC6) or sodium dodecanoate (NaC12) with octanoic acid (C8), nonanoic acid (C9) or decanoic acid (C10). For the DES containing NaC6, the molar fraction of acid (X_{acid}) in the system was 0.7, and for the DES containing NaC12, X_{acid} was 0.8 [6,7].

All MD simulations were performed using GROMACS package, and the molecules were represented using the OPLS-AA force field [8-10]. After the conclusion of production simulations, the results were analyzed through visual observation, analysis of hydrogen bonding, radial distribution functions (RDF), calculation of densities and diffusion coefficients [8].

The results showed that MD simulations can be successfully employed as a tool to predict the formation of DES, and to better understand the molecular interactions that occur in these solvents. A proposal of DES's conformation was made, based on a global discussion of the results, supported mainly by the RDF analysis. It was concluded that the sodium cation plays a major role in the arrangement of molecules.

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