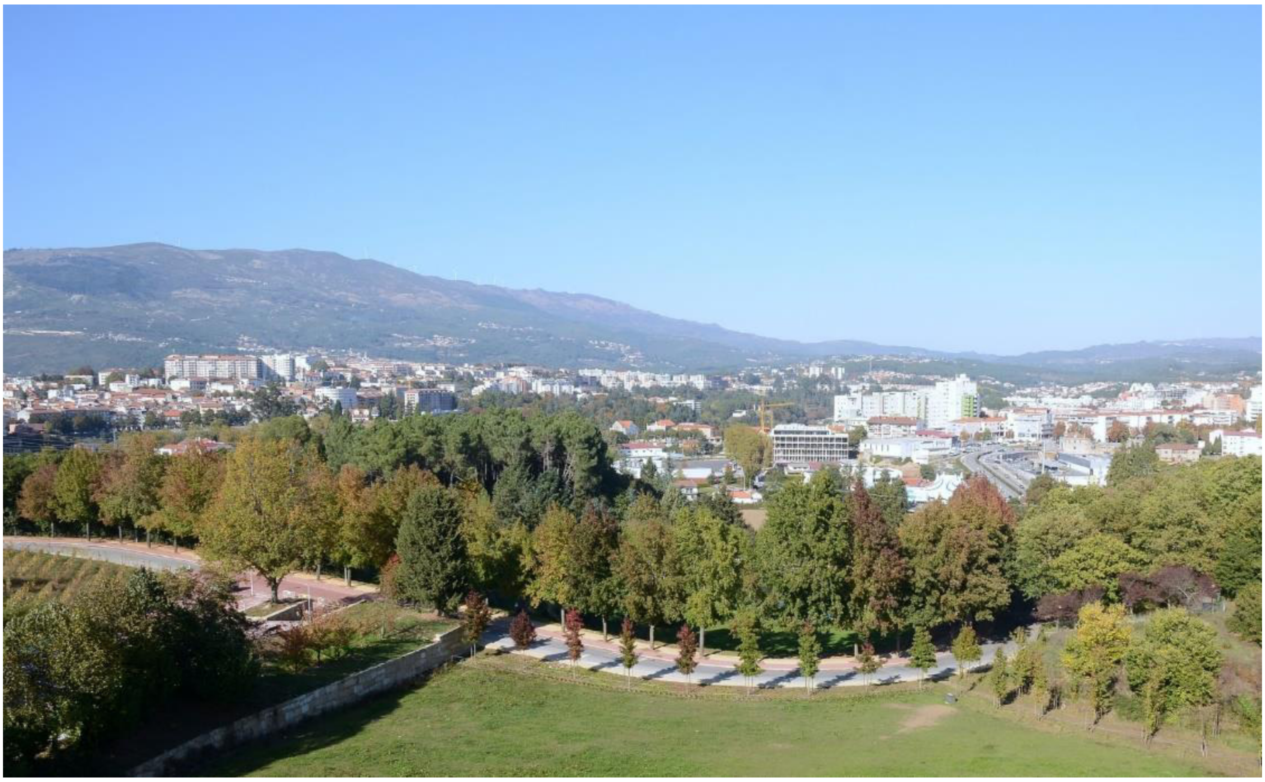
8PYCheM

Portuguese Young Chemists Meeting

17-19 May 2023 Vila Real



UNIVERSIDADE DE TRÁS-OS-MONTES E ALTO DOURO

17th-19th may 2023

Vila Real, Portugal

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

Title	Livro de Resumos do 8th Portuguese Young Chemists Meeting
Authors	Céu Sousa, Vanessa Gomes, Mariana Fernandes, Vânia Graça
Support	Electronics
Support detail	PDF
Edition	1st Edition
Bar Code	ISBN 978-989-8124-38-8 9 789898 124388
Editor	Sociedade Portuguesa de Química
Country	Portugal
E-mail	secretariado@spq.pt
Editor Prefix	978-989-97667

INSTITUTIONAL SUPPORT

SOCIEDADE PORTUGUESA DE QUÍMICA

GQJ
Grupo de Químicos Jovens

utad
UNIVERSIDADE
DE TRÁS-OS-MONTES
E ALTO DOURO

CQ VR
CENTRO
DE QUÍMICA
VILA REAL

AL EU
VILA REAL

PLATINUM

Lema d'Origem

SILVER SPONSOR

Chemistry A European Journal
Chemistry Europe

solitica
SOLUÇÕES ANALÍTICAS, LDA.

Dias de Sousa
INSTRUMENTAÇÃO ANALÍTICA E CIENTÍFICA, S.A.

BRONZE SPONSOR

NORLEQ
NORLEQ - Equipamentos e Serviços

LABOR
SPIRIT, Lda.

OTHER SPONSORS

AZEITE
PORCA DE
MURÇA

ADEGA DE
FAVAIOS
SINCE 1952

ADEGA
VILA REAL
ANO 1955

enzymatic

TABLE OF CONTENTS

Committees

WELCOME MESSAGE

On behalf of the organizing committee, we extend our warmest welcome to all the participants in the 8th Portuguese Young Chemistry Meeting (8th PYCheM). 8thPYChem is a conference gathering young scientist to share their research results, new ideas and motivation.

This biennial conference, dating back to 2008, is dedicated to gather young researchers from all subfields of Chemistry, as well as other related scientific areas of Research.

Young chemists and researchers from any nationality are particularly encouraged to share their scientific highlights amongst their peers from chemical sciences, expand their international research network and attend lectures from recognized experts in various fields of Chemistry.

The 8th PYCheM will count with 5 plenary lectures, 5 keynote lectures, 6 invited lectures, 24 oral communications, 10 flash oral communications and 2 poster sessions with over 61 poster communications. In addition, a workshop highlighting the importance of open science and data will have place.

The Portuguese Young Chemists Award (PYCA) attributed by The Young Chemists Group (GQJ) from SPQ aims to promote excellence in Chemistry developed by young researchers, with particular focus on the scientific impact on the Society. This 7th edition of the PYCA award is kindly sponsored by SPQ.

Vila Real, situated in the North region of Portugal, it is a largest city of the Vila Real District. It holds the central position within the Douro intermunicipal community and the Trás-os-Montes e Alto Douro historical province. The city is located in a plateau high, over the promontory formed by the gorges of the Corgo and Cabril rivers, where the oldest part of town (Vila Velha) is located, framed by the escarpments of the Corgo gorge.

We hope you will find these three days to be an informative, stimulating and pleasant time in this conference.

Welcome Vila Real

Welcome to the 8thPYCheM

The Organizing Committee

COMMITTES

Organizing committee

Céu Sousa
Mariana Fernandes
Vanessa Gomes
Vânia Graça

Local Staff

Abderrazzak Ait Bassou
Ana Rita Queijo
Ana Rita Moura
Ana Gomes
Andreia Veloso
Leonilde Marchão
Monica Silva
Nuno Jorge

Scientific committee

António Jordão (Instituto Politécnico de Viseu)
Verónica Bermudez (Universidade de Trás-os-Montes e Alto Douro)
Maria Inês Dias (instituto Politécnico de Bragança)
Sandra Nunes (Universidade de Coimbra)
Artur Silva (universidade de Aveiro)
Sérgio Rodrigues (Universidade de Coimbra)
Maria Ermelinda Eusébio (Universidade de Coimbra)
Samuel Silvestre (Universidade da Beira Interior)
António Parola (Universidade Nova de Lisboa)
Maria Manuela Silva (Universidade do Minho)
Fernando Nunes (Universidade de Trás-os-Montes e Alto Douro)
Eduardo Marques (Universidade do Porto)
João Mano (Universidade de Aveiro)
José Prata (Instituto Politécnico de Lisboa)
Rosário Domingues (Universidade de Aveiro)

Secretariat

Leonardo Mendes
Cristina Campos

GENERAL INFORMATION

Registration desk

Wednesday, 17 May 2023 (8:30 at 18:00)

Thursday, 18 May 2023, (8:30 at 13:00)

Friday, 19 May 2023, (8:30 at 13:00)

Coffee breaks

Coffee breaks will be held at main in the Geosciences Building

Conference Language

English is the official language of the conference. No simultaneous translation is available.

Internet

The Auditorium have a free wireless Internet connection.

Parking

UTAD is an eco-campus. The campus parks are shared with the community so the parking spaces are subject to availability.

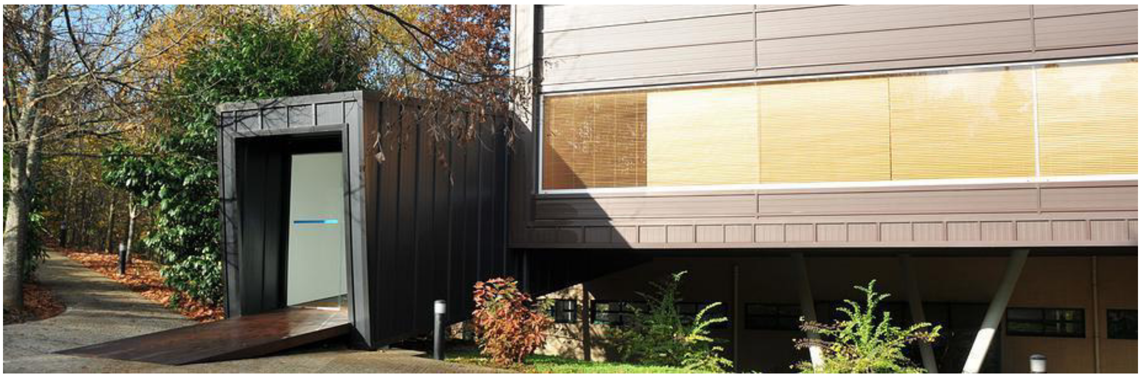
Program changes

Last minutes changes to the program may be unavoidable.

SOCIAL PROGRAM

- **Porto de Honra/Port of Honor**

The Porto de Honra/Port of Honor will be served at the Panoramic Restaurant at the University of Trás-os-Montes and Alto Douro in the first day of congress (May 17th) at 18:00.



- **Congress Dinner**

The Conference Dinner will take place at the Hotel Miracorgo, on the 18th of may at 20:30.

AWARDS

PYCA

The Portuguese Young Chemists Award (PYCA) attributed by the Young Chemists Group (GQJ) aims to promote excellence in Chemistry developed by young researchers, with particular focus on the scientific impact on the society. The prize is awarded every two years to recent doctors with less than 35 years and laureates the work done during their PhD. It is open to Portuguese or foreigner young researchers that received the PhD degree in any field of the chemical sciences from a Portuguese University.

Supported by:

SOCIEDADE PORTUGUESA DE QUÍMICA

BEST ORAL COMMUNICATION AWARD

CAPP micropipette

Inscription in 9th PYCheM

Supported by:

solítica SOLUÇÕES ANALÍTICAS, LDA.

SOCIEDADE PORTUGUESA DE QUÍMICA

BEST FLASH COMMUNICATION AWARD

Enzymatic Products

Inscription in 9th PYCheM

Supported by:

enzymatic

SOCIEDADE PORTUGUESA DE QUÍMICA

- **BEST POSTER COMMUNICATION AWARD**

Inscription in 9thPYCheM

Supported by:

SOCIEDADE PORTUGUESA DE QUÍMICA

SCIENTIFIC INFORMATION

Oral communications

The oral communications are divided into:

- PL| Plenary sessions (45 minutes for presentation, plus 5 minutes for Q&A).
- KN| Keynote (25 minutes for presentation, plus 5 minutes for Q&A).
- IL| Invited Oral Communications (15 minutes for presentation, plus 5 minutes for Q&A).
- O| Oral Communications (10 minutes for presentation, plus 5 minutes for Q&A).
- F| Flash Communications (5 minutes for presentation)

NOTE: To **all participants presenting oral and flash communications**, it is kindly asked to **contact one organization member 24 hours** in advance at the reception desk to deliver your PowerPoint presentation (videos must be inserted in power point).

Poster exhibition

The poster exhibition will be located in the main Hall in the Geosciences Building

The posters should be mounted after lunch time and taken down at the end of the day. All posters should be formatted vertically of standard A0. The authors should be present nearby the corresponding poster during the poster sessions.

Poster panel will be arranged numerically and distributed by two poster sessions.

- **Poster Session 1**: Wednesday 17th Poster Session: 16:00-16:45 (P1-P30)
- **Poster Session 2**: Thursday 18th Poster Session: 15:50-16:40 (P31-P61)

Each participant will be able to vote in the “best poster presentation”. The vote will be submitted online.

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

Hours	17th May (Wednesday)	Hours	18th May (Thursday)	Hours	19th May (Friday)
8:30	**Registration**	9:00	**PL3 Charis M. Galanakis**	9:00	**PL5 Maria Helena Braga**
9:30	**Opening Ceremony**	9:50	**IL3 Carla Vitorino**	9:50	**O16 Daniela Pinheiro**
10:00	**PL 1 Christian Griesinger**	10:10	**O8 Leonilde Marchão**	10:05	**O17 Pedro Matias**
10:50	**Coffee break**	10:25	**O9 Artur Bento**	10:20	**O18 Tiago Duarte**
11:05	**KN 1 Xavier Cattoen**	10:40	**Coffee break**	10:35	**Coffee break**
11:35	**O1 Renata Amaral**	10:55	**KN3 Lillian Barros**	10:50	**KN5 Maria José Tapia**
11:50	**O2 Alexandre Alves**	11:25	**IL4 Mafalda Sarraguça**	11:20	**IL5 Leonor Ferreira**
12:05	**O3 Luís Filipe**	11:45	**O10 Joana Madureira**	11:40	**O19 Sérgio Silva**
12:20	**O4 Mafalda Penetra**	12:00	**O11 Maria Leichtweis**	11:55	**O20 Ana Silva**
12:35	**F1 Filipa Teixeira**	12:15	**F6 Edgar Silva-Santos**	12:10	**IL6 Tânia Albuquerque**
12:40	**F2 Carlos Shiraishi**	12:20	**F7 Filipa Mandim**	12:30	**O21 Alexis Pereira**
12:45	**F3 Karina Silvério**	12:25	**F8 Thauane Silva**	12:45	**O22 Sandra Marcelino**
12:50	**F4 Ana Queijo**	12:30	**F9 Zoé Arnaut**	13:00	**Lunch**
12:55	**F5 Nuno Jorge**	12:35	**F10 Daniela Ferreira**	14:15	**023 Filipe Santos**
13:05	**Lunch**	12:45	**Lunch**	14:30	**024 Artur Farinha**
14:20	**PL2 António Candeias**	14:00	**PL4 João Paulo André**	14:45	**2nd National Retrosynthesis Competition 2023 Award**
15:10	**IL1 Isabel Soares**	14:50	**O12 Fátima Gonçalves**		
15:30	**O5 Rui Sousa**	15:05	**O13 Samuel Mugo**	15:45	**EYCN – Joana Madureira**
15:45	**O6 Mariana Monteiro**	15:20	**O14 José Ferraz-Caetano**	16:00	**IYCN – João Borges**
16:00	**Coffee break/Poster session**	15:35	**O15 Luís Viegas**	16:15	**PYCA Award**
16:45	**KN2 Sérgio Sousa**	15:50	**Coffee break/Poster session**	16:30	**Best Oral, flash and Poster Awards**
17:15	**IL2 João Rodrigues**	16:40	**KN4 João Salvador**	16:45	**Next conference**
17:35	**O7 Joana Ferreira**	17:10	**Workshop Pedro Mendes**	17:00	**Closing Ceremony**
18:00	**Port of Honor**	18:40	**GQJ Assembly**		
		20:30	**Conference dinner**		

PL – Plenary
KN – Keynote
O – Oral communication

F – Flash communication
IL – Invited lecture
GQJ – Grupo de Químicos Jovens

EYCN – European Young Chemists Network
IYCN – International Younger Chemists Network
PYCA – Portuguese Young Chemists Award

WEDNESDAY 17TH MAY

	Chair: Mariana Fernandes (Universidade de Trás-os-Montes e Alto Douro)
9:30	Open Ceremony
	Chair: Marta Piñeiro (Universidade de Coimbra)
10:00	**PL1** Christian Griesinger (Max Planck Institute for Multidisciplinary Sciences) *Small molecules triggering transmembrane signaling and interfering with aggregation important in neurodegeneration*
10:50	Coffee Break
	Chair: José Prata (Instituto Superior de Engenharia de Lisboa/Instituto Politécnico de Lisboa) **Young chair**: Joana Madureira (Instituto Superior Técnico)
11:05	**KN1** Xavier Cattoën (CNRS – Universidade Grenoble-Alpes) Mesoporous (organo)silica nanoparticles for drug delivery
11:35	**O1** Renata Amaral (Universidade de Aveiro) *High-pressure pre-treatment to tailor starch-based films properties?*
11:50	**O2** Alexandre Alves (Faculdade de Ciências da Universidade do Porto) *Confined silver nanoparticles in ionic liquid films*
12:05	**O3** Luis Filipe (Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa FCT-NOVA) *In vitro antimicrobial studies of mesoporous silica nanoparticles comprising anionic ciprofloxacin ionic liquids and organic salts*
12:20	**O4** Mafalda Penetra (Universidade de Coimbra) *Unraveling the mechanisms of cellular permeation of LUZ51*
12:35	**F1** Filipa Teixeira (LAQV-REQUIMTE, Instituto Superior de Engenharia do Porto - Instituto Politécnico do Porto) *Microparticles containing Actinidia arguta extracts prepared by spray drying*
12:40	**F2** Carlos Shiraishi (CIMO, Instituto Politécnico de Bragança) *Fig (Ficus carica L.) bioresidues as a source of bioactive compounds: A sustainable approach*
12:45	**F3** Karina Silvério *Efficiency of chemical precipitation technique in the removal of organic matter from industrial effluent of slaughterhouse*
12:50	**F4** Ana Queijo (Universidade de Trás-os-Montes e Alto Douro) *Pharmaceuticals' mixtures: evaluation of its electrochemical qualitative separation*
12:55	**F5** Nuno Jorge (Universidade de Trás-os-Montes e Alto Douro) *Treatment of agro-industrial wastewater: batch vs continuous system*
13:05	Lunch

	Chair: Verónica de Zea Bermudez (Universidade de Trás-os-Montes e Alto Douro) **Young Chair**: Mafalda Sarraguça (LAQV@REQUIMTE, Faculdade de Farmácia da Universidade do Porto)
14:20	**PL2** António Candeias (Universidade de Évora) *Multianalytical approaches for the study and conservation of cultural heritage - the hercules lab experience*
15:10	**IL1** Maria Isabel Soares (Universidade de Coimbra) *Generation of molecular diversity via lewis base-catalyzed reactions of chromane scaffolds and allenoates*
15:30	**O5** Rui Sousa (Universidade do Minho) *New developments in biocide chemosensors: are quinoline-based hydrazones any good?*
15:45	**O6** Mariana Monteiro (Faculdade de Farmácia, Universidade de Lisboa) *Synthesis of Imidazolidinones through Pd-catalyzed Cycloaddition of Bicyclic Aziridine with Isocyanates*
16:00	Coffee Break/Poster session
	Chair: Rosário Domingues (Universidade de Aveiro)
16:45	**KN2** Sérgio Sousa (UCIBIO-REQUIMTE, Universidade Porto) *Combining multi-level biomolecular simulations with experimental data for drug discovery*
17:15	**IL2** João Rodrigues (Universidade de Aveiro) *Exploiting the Chemical Modifications of Laminarin to Develop Tunable Biomaterials for Biomedical Applications*
17:35	**O7** Joana Ferreira (Universidade de Aveiro) *A facile metal-catalyzed approach towards functionalized azaindoles*
18:00	Port of Honor

THURSDAY 20TH MAY

	Chair: Fernando Nunes (universidade de Trás-os-Montes e Alto Douro) **Young Chair:** Rui Sousa (Universidade do Minho)
9:00	**PL3** Charis M. Galanakis (Galanakis Laboratories L.P.) *Innovations, technology disruptions and target interventions for future food*
9:50	**IL3** Carla Vitorino (Faculdade de Farmácia, Universidade de Coimbra) *Strategies to address hard-to-access brain tumors using solid lipid nanoparticles*
10:10	**O8** Leonilde Marchão (Universidade de Trás-os-Montes e Alto Douro)

Cultivation of chlorella vulgaris in winery wastewater for nutrient removal and biomass production

10:25 **O9** Artur Bento (Instituto de Tecnologia Química e Biológica António Xavier – Universidade Nova de Lisboa)
Sequential processing of Pinus radiata bark with scCO2 and an ionic liquid catalyst yields abundant resin acids and alkanoic acids enriched in suberin

10:40 Coffee Break

Chair: António Jordão (Instituto politécnico de Viseu)
Young Chair: Carolina Jesus (Universidade de Coimbra)

10:55 **KN3** Lillian Barros (CIMO, Instituto Politécnico de Bragança)
From nature to products: natural food ingredients applications

11:25 **IL4** Mafalda Sarraguça (LAQV@REQUIMTE, Faculdade de Farmácia da Universidade do Porto)
Towards a greener pharmaceutical industry. this is the way!

11:45 **O10** Joana Madureira (Instituto Superior Técnico)
Optimization of ultrasound- and heat-assisted extractions of phenolic compounds from olive wastes for food applications

12:00 **O11** Maria Leichtweis (CIMO, Instituto Politécnico de Bragança)
Evaluation of the phenolic profile and bioactive potential of portuguese and algerian pumpkin by-products

12:15 **F6** Edgar Silva-Santos (Faculdade de Ciências da Universidade do Porto)
A computational study on the hydrosilylation of imines

12:20 **F7** Filipa Mandim (CIMO, Instituto Politécnico de Bragança)
Phenolic Composition and in vitro Bioactivities of Cardoon Blades: Study of its Potential as a Functional Ingredient

12:25 **F8** Thauane Silva (Universidade de Coimbra)
Synthesis and characterization of monolith silica/fiber aerogel for water adsorption

12:30 **F9** Zoé Arnaut (Universidade de Coimbra)
Gold tris-binol menthol monophosphite for the preparation of phenol derivatives

12:35 **F10** Daniela Ferreira (Faculdade de Farmácia da Universidade de Lisboa)
Synthesis and biological activity of new bisquinolizidine derivatives from bio renewable resources

12:45 Lunch

Chair: Maria José Tapia (Universidade de Burgos)
Young Chair: Sandra Nunes (Universidade de Coimbra)

14:00	**PL4** João Paulo André (Universidade do Minho) *Domestic science – a historical curiosity in chemistry education*
14:50	**O12** Fátima Gonçalves (Faculdade de Ciências da Universidade do Porto) *Optimization of a GDME-HPLC-DAD-MS/MS methodology for the screening of volatile carbonyl compounds in wood-based panels*
15:05	**O13** Samuel Mugo (Universidade MacEwan) *Paper based point of need (pon) colorimetric and multiplexed electrochemical smartphone based sensors for citizen chemical sensing analytics*
15:20	**O14** José Ferraz-Caetano (LAQV-REQUIMTE - Faculdade de Ciências da Universidade do Porto) *Explainable Artificial Intelligence methods in Machine Learning models to predict thermodynamic properties through vaporization enthalpies*
15:35	**O15** Luis Viegas (Centro Química de Coimbra – Instituto de ciências moleculares) *Degradation of fluorinated compounds in the troposphere: an accurate computational protocol*
15:50	Coffee break/Poster session
	Chair: Xavier Cattoen (CNRS – Universidade Grenoble-Alpes)
16:40	**KN4** João Salvador (Instituto Superior Técnico, Universidade de Lisboa) *Corrosion - Materials and Environment*
17:10	**Workshop** Pedro Mendes (Instituto Superior Técnico) *Crash course on open science and data*
18:40	GQJ Assembly
20:30	Conference dinner

FRIDAY 19TH MAY

	Chair: Pedro Tavares (Universidade de Trás-os-Montes e Alto Douro) **Young Chair:** João Borges (Universidade de Aveiro)
9:00	**PL5** Maria Helena Braga (Faculdade de Engenharia da Universidade do Porto) *The very latest in solid-state batteries: the condensed matter or quantum battery*
9:50	**O16** Daniela Pinheiro (Universidade de Trás-os-Montes e Alto Douro) *Electrochromic windows based on luminescent acrylate/ionosilicas*
10:05	**O17** Pedro Matias (Universidade de Coimbra) *Reduced chitosan as an adsorbent for metal ion removal from water*
10:20	**O18** Tiago Duarte (Universidade de Trás-os-Montes e Alto Douro) *Silk fibroin-based thermotropic device*
10:35	Coffee Break

	Chair: Paula Branco (NOVA School of Science and Technology, Universidade NOVA de Lisboa) **Young Chair**: Maria Inês Dias (CIMO, Instituto Politécnico de Bragança)
10:50	**KN5** Maria José Tapia (Universidade de Burgos) *Luminescence with professor burrows. playing with lanthanoids and conjugated polyelectrolytes*
11:20	**IL5** Leonor Ferreira (Associação Fraunhofer Portugal Research) *Turning wastewaters into a valuable resource*
11:40	**O19** Sérgio Silva (Universidade de Trás-os-Montes e Alto Douro) *The effect of oleate in the biological nitrogen removal*
11:55	**O20** Ana Silva (LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto) *Petscent project: obtaining optical sensors from pet bottles*
12:10	**IL6** Tânia Albuquerque (Instituto Nacional de Saúde Doutor Ricardo Jorge, I.P.) *Are melon by-products a suitable source of nutrients and bioactive compounds for the development of functional foods?*
12:30	**O21** Alexis Pereira (CIMO, Instituto Politécnico de Bragança) *Exploiting the nutritional and chemical diversity of Portuguese tomato (Solanum lycopersicum L.) germplasm*
12:45	**O22** Sandra Marcelino (Universidade de Vigo) *Pomegranate leaf extracts characterization and their potential use as a functional ingredient*
13:00	Lunch
	Chair: Mariana Fernandes (Universidade de Trás-os-Montes e Alto Douro)
14:15	**O23** Filipe Santos (Universidade da Beira Interior) *Algae biomass as precursors for preparation of multicomponent luminescent systems containing carbon dots and natural pigments*
14:30	**O24** Artur Farinha (Faculdade de Ciências da Universidade do Porto) *Ionic liquids in confined spaces*
	Chair: Maria do Amparo Faustino (Universidade de Aveiro)
	2nd National Retrosynthesis Competition 2023 Award
	Chair: Maria do Amparo Faustino
14:45	**Metil Etil Propil**: Alexandre P. Felgueiras; Vitaliy Masliy; Zoe A. Arnaut
15:00	**XICO XICO**: Ricardo Santos
15:15	**ChemAveiro**: Manuel Verganista, Telmo Francisco

	Chair: Mariana Fernandes (Universidade de Trás-os-Montes e Alto Douro)
15:30	Joana Madureira ((Instituto Superior Técnico) EYCN (European Young Chemists Network)
15:45	João Borges (Universidade de Aveiro) The International Younger Chemists Network (IYCN): Connecting, Supporting, Advocating and Empowering Younger Chemists Globally”
16:00	PYCA (Portuguese Young Chemists Award) Pedro Brandão (Egas Moniz - School of Health and Science) *“Putting all the pieces together”: isatin-based multicomponent reactions as a sustainable approach in drug discovery*
16:15	Delivery of the Retrosynthesis award: Jury: Maria Manuela Marques Raposo (UM); Maria Emília Sousa (FFUP); Paula Branco (NOVA-FCT). Delivery of the Best Oral Award Delivery of the Best Flash Awards Delivery of the Best Poster Awards
16:30	PYCHeM 2025 presentation
16:45	Closing Ceremony

LIST OF COMMUNICATIONS

Plenary Lectures

- **PL1** - Christian Griesinger
  Small molecules triggering transmembrane signaling and interfering with aggregation important in neurodegeneration

- **PL2** - António Candeias
  Multianalytical approaches for the study and conservation of cultural heritage - the hercules lab experience

- **PL3** - Charis M. Galanakis
  Innovations, technology disruptions and target interventions for future food

- **PL4** - João Paulo André
  Domestic science – a historical curiosity in chemistry education

- **PL5** - Maria Helena Braga
  The very latest in solid-state batteries: the condensed matter or quantum battery

Keynotes

- **KN1** - Xavier Cattoën
  Mesoporous (organo)silica nanoparticles for drug delivery

- **KN2** - Sérgio Sousa
  Combining multi-level biomolecular simulations with experimental data for drug discovery

- **KN3** - Lillian Barros
  From nature to products: natural food ingredients applications

- **KN4** - João Salvador
  Corrosion - Materials and Environment

- **KN5** - Maria José Tapia
  Luminescence with professor burrows. playing with lanthanoids and conjugated polyelectrolytes

Invited Lecture

- **IL1** - Maria Isabel Soares
  Generation of molecular diversity via lewis base-catalyzed reactions of chromane scaffolds and allenoates

- **IL2** - João Rodrigues
  Exploiting the chemical modifications of laminarin to develop tunable biomaterials for biomedical applications

- **IL3** - Carla Vitorino
  Strategies to address hard-to-access brain tumors using solid lipid nanoparticles

- **IL4** - Mafalda Sarraguça
  Towards a greener pharmaceutical industry. this is the way!

- **IL5 -** Leonor Ferreira
  Turning wastewaters into a valuable resource

- **IL6** - Tânia Albuquerque
  Are melon by-products a suitable source of nutrients and bioactive compounds for the development of functional foods?

Oral Communication

- **O1** - Renata Amaral
  High-pressure pre-treatment to tailor starch-based films properties?

- **O2** - Alexandre Alves
  Confined silver nanoparticles in ionic liquid films

- **O3** - Luis Filipe
  In vitro antimicrobial studies of mesoporous silica nanoparticles comprising anionic ciprofloxacin ionic liquids and organic salts

- **O4** - Mafalda Penetra
  Unraveling the mechanisms of cellular permeation of LUZ51

- **O5** - Rui Sousa
  New developments in biocide chemosensors: are quinoline-based hydrazones any good?

- **O6** - Mariana Monteiro
  Synthesis of imidazolidinones through pd-catalyzed cycloaddition of bicyclic aziridine with isocyanates

- **O7** - Joana Ferreira
  A facile metal-catalyzed approach towards functionalized azaindoles

- **O8** - Leonilde Marchão
  Cultivation of *Chlorella vulgaris* in winery wastewater for nutrient removal and biomass production

- **O9** - Artur Bento
  Sequential processing of *Pinus radiata* bark with $scCO_2$ and an ionic liquid catalyst yields abundant resin acids and alkanoic acids enriched in suberin

- **O10** - Joana Madureira
  Optimization of ultrasound- and heat-assisted extractions of phenolic compounds from olive wastes for food applications

- **O11** - Maria Leichtweis
  Evaluation of the phenolic profile and bioactive potential of portuguese and algerian pumpkin by-products

- **O12** - Fátima Gonçalves
  Optimization of a GDME-HPLC-DAD-MS/MS methodology for the screening of volatile carbonyl compounds in wood-based panels

- **O13** - Samuel Mugo
  Paper based point of need (pon) colorimetric and multiplexed electrochemical smartphone based sensors for citizen chemical sensing analytics

- **O14** - José Ferraz-Caetano
  Explainable Artificial Intelligence methods in Machine Learning models to predict thermodynamic properties through vaporization enthalpies

- **O15** - Luis Viegas
  Degradation of fluorinated compounds in the troposphere: an accurate computational protocol

- **O16** - Daniela Pinheiro
  Electrochromic windows based on luminescent acrylate/ionosilicas

- **O17** - Pedro Matias
  Reduced chitosan as an adsorbent for metal ion removal from water

- **O18** - Tiago Duarte
  Silk fibroin-based thermotropic device

- **O19** - Sérgio Silva
  The effect of oleate in the biological nitrogen removal

- **O20** - Ana Silva
  Petscent project: obtaining optical sensors from pet bottles

- **O21** - Alexis Pereira
  Exploiting the nutritional and chemical diversity of Portuguese tomato (*Solanum lycopersicum* L.) germplasm

- **O23** - Filipe Santos
  Algae biomass as precursors for preparation of multicomponent luminescent systems containing carbon dots and natural pigments

- **O24** - Artur Farinha
  Ionic liquids in confined spaces

Flash communication

- **F1** - Filipa Teixeira
  Microparticles containing *Actinidia arguta* extracts prepared by spray drying

- **F2** - Carlos Shiraishi
  Fig (*Ficus carica* L.) bioresidues as a source of bioactive compounds: A sustainable approach

- **F3** - Karina Silvério
  Efficiency of chemical precipitation technique in the removal of organic matter from industrial effluent of slaughterhouse

- **F4** - Ana Queijo
  Pharmaceuticals' mixtures: evaluation of its electrochemical qualitative separation

- **F5** - Nuno Jorge
  Treatment of agro-industrial wastewater: batch vs continuous system

- **F6** - Edgar Silva-Santos
  A computational study on the hydrosilylation of imines

- **F7** - Filipa Mandim
  Phenolic composition and *in vitro* bioactivities of cardoon blades: study of its potential as a functional ingredient

- **F8** - Thauane Silva
  Synthesis and characterization of monolith silica/fiber aerogel for water adsorption

- **F9** - Zoé Arnaut
  Gold tris-binol menthol monophosphite for the preparation of phenol derivatives

- **F10** - Daniela Ferreira
  Synthesis and biological activity of new bisquinolizidine derivatives from bio renewable resources

Poster Communication

Medicinal chemistry

- **P1** - Ana P. Martins
  Hyperbaric storage as a cell preservation methodology – can blood be stored under pressure?

- **P2** - Margarida M. Cordeiro
  Analysis of different methods to calculate permeability coefficients

- **P3** - Joana Cardoso
  New trojan horses designed to overcome antifungal resistance

- **P4** - Mariana C. Almeida
  Synthesis of siderophore mimetics and conjugation with antibacterial adjuvants for medicinal and environmental applications

- **P5** - Ana Beatriz Pereira
  New chiral 6,7-bis(hydroxymethyl)-1h,3h-pyrrolo[1,2-c]thiazoles as p-53 activating agents for colorectal cancer targeted therapy

- **P6** - Adelino M. R. Pereira
  Exploring the Pyrrolo[1,2-c]thiazole Scaffold: Design of novel p53-activating agents for colorectal cancer therapy

- **P7** - Chrislaura Carmo
  Bodipy dyes for photodynamic therapy of cancer

Computational chemistry

- **P8** - Maria Leonor Frazão
  Correlating zeolite characteristics with synthesis conditions: From comprehensive datasets to machine learning models

- **P9** - Helena Vendas
  Estimation of droplets diameter in a liquid-liquid extraction column using image processing methods

- **P10** - Roberto Pinto
  New Antidotes for *Bothrops asper* venom: study of PLA2 protein

- **P11** - Dário Cartaxo
  Molecular descriptors for the characterization of antibiotics: combining machine learning and ab initio calculations

- **P12** - Tânia Cova
  Characterizing emerging psychoactive drugs by mining chemical data and using molecular simulations

- **P13** - Sandra C. C. Nunes
  DNA nanostructures as antimicrobial drug nanocarriers: a molecular dynamics study

- **P14** - João Miguel Inácio
  In silico development of novel polymyxin b derivatives: qsar models of antimicrobial activity

- **P15** - Andreia P. Fonseca
  Greenhouse gases solubility by magnetic ionic liquids: MD simulation study

Electrochemistry

- **P16** - Eduarda Pereira
  Toxic dinoflagellates (*Dinophysis* spp.) detection by genosensors and molecular biomolecular approaches

Food Chemistry

- **P17** - Daniela Oliveira
  Development and characterization of solid lipid nanoparticles formulations in nutrients delivery for animal feed

- **P18** - Gabriel Azevedo
  Obtention and characterization of a polyphenol enriched extract from olive pomace

- **P19** - Beatriz H. Paschoalinotto
  Impact of ammoniacal nitrogen on the centesimal composition and chemical profile of *portulaca oleracea* l.

- **P20** - Felipe Macedo Alves
  Natural coating formulations to preserve chestnuts

- **P21** - Roberto A. Costa
  Selenium biofortification of plants and mushrooms: towards healthier foods for human nutrition – an overview

- **P22** - Joana P. B. Rodrigues
  Vegetables losses and wastes as a source of bio based ingredients

- **P23** - António M. Jordão
  Evaluation of phenolic extraction method on the antioxidant capacity estimation of red grapes at different stages of maturation

Green chemistry

- **P24** - Margarida I. M. Esteves
  Synthesis of amino acid-based surfactants through the valorisation of used cooking oils

- **P25** - Cátia Ferreira
  Extraction of bioactive compounds from grape pomace using deep eutectic solvents

- **P26** - Inês C. P. Escobar
  Bioplastics from used cooking oil

- **P27** - Margarida L. Almeida
  Formaldehyde emissions in wood-based panels – relationships between test methods

- **P28** - Gabriel Lamino Camilo
  Study of biodiesel production from waste cooking oil by ethyl transesterification and its purification with the use of activated carbons derived from olive pits

- **P29** - Eduardo Candido Milani
  Valorization of oliviculture residues for the removal of estrogens from water

- **P30** - Inês Correia
  Exploring the synergies of 3D-printed biochar-inorganic polymer composite as an effective CO_2 adsorbent

Materials chemistry and Nanomaterials

- **P31** - Simão Pinho
  Iron nanofertilizers for the development of sustainable soybean crops

- **P32** - Daniela R. P. Loureiro
  Ceftriaxone-loaded lipid nanoparticles to treat prosthetic joint infections caused by *S. aureus*

- **P33** - Cátia S. M. Esteves
  Biopolymers as shell materials for microcapsules

- **P34** - Abderrazzak Ait Bassou
  Deposition of h-lumno3 thin films by mocvd: growth and structural characterization

- **P35** - Andreia D. Veloso
  The dialysis effect: insights on the role of purification processes in the properties of carbon nanomaterials

- **P36** - Carolina F. Jesus
  Production of eco-materials from forest residues to replace conventional plastics

- **P37** - Inês S. Marques
  Biomass-derived (electro)catalysts for sustainable processes

- **P38** - Gabriela Coelho
  Aminated silica from rice husk towards luminescent lanthanide materials

- **P39** - Renata Matos
  High performance electrocatalysts derived from shrimp shells towards oxygen reduction

- **P40** - Francisco Vicente
  Optimizing crab shell properties for enhanced co$_2$ adsorption

- **P41** - Juliana Araújo
  Synthesis and characterization of iron-based metal-organic frameworks from terephthalic acid derivatives for biomedical applications

- **P42** - Francisco J.P.M. Sousa
  Influence of reinforcing fiber’s particle size in pbs-based composites

Analytical chemistry

- **P43** - Cláudio M. R. Almeida
  Lanthanide doped silica-based film as a sensor for amines vapours detection and discrimination

- **P44** - Rui Figueiredo
  MIP nanoparticles for specific recognition of BSA

Biochemistry

- **P45** - Ana R. Teixeira
  Treatment of olive washing water by coagulation-flocculation-decantation and UV-A/Fenton

- **P46** - Raquel Vieira
  The effect of a stressful stimulus in behavioural, metabolic and biochemical markers in zebrafish

- **P47** - Ana Gomes
  Inactivation of *Aspergillus brasiliensis* spores in water using advanced oxidation processes

- **P48** - Mónica G. Silva
  Antioxidant and mitochondrial bioenergetic responses to microplastic toxicity: the influence of diet

Chemistry of Natural Products

- **P49** - José R. A. Coelho
  New potential insecticide candidates based on eugenyl 3-aminobenzoates

- **P50** - Volodymyr Tkach
  Poisonous mushrooms as a renewable font for green conducting polymers. a theoretical view

Organic chemistry

- **P51** - Telmo N. Francisco
  Synthesis of Symmetrical and Non-Symmetrical Nitrobenzenes from 3-Formylchromones

- **P52** - Ricardo A. L. S. Santos
  The instability of π-bonds after the nitrone's o-additions and [3+2]-cycloadditions

- **P53** - Abdullahi A. Muiz
  Functionalization of natural bisquinolizidine alkaloids

- **P54** - Duarte B. Clemente
  Electrochemical cyanation of sparteine in continuous flow

- **P55** - João A. Pacheco
  Increasing complexity of quinic acid by photoredox catalysis

- **P56** - Manuel José Verganista Alves
  Synthesis and catalytic studies of iron tricarbonyl cyclopentadienones on hydrogen borrowing amination of cyclitols

- **P57** - João V.R. Gonçalves
  Novel spiro-penicillanates from 6-alkylidenepenicillanates via formal cycloadditions of allenoates and dimethylsulfonium ylides

- **P58** - Vitor A. S. Almodovar
  Synthesis and structural and photophysical characterizations of Diketopyrrolopyrroles for technical and biological applications

- **P59** - Carla Cunha
  Efficient design of di-tert-butly-diphenyldibenzofulvene derivatives with enhanced aggregation-induced emission

Physical chemistry

- **P60** – Miguel Teixeira
  Sorption study of furanic compounds in transformers' insulating materials systems

Surface chemistry and interfaces

- **P61** - Nélia C. T. Tavares
  Essential oils and their emulsions: gathering antibacterial activity and molecular dynamics in unveiling new antiseptic cosmetics

PYCA AWARD

- Pedro Brandão
  "Putting all the pieces together": isatin-based multicomponent reactions as a sustainable approach in drug discovery

PLENARY LECTURES

SMALL MOLECULES TRIGGERING TRANSMEMBRANE SIGNALING AND INTERFERING WITH AGGREGATION IMPORTANT IN NEURODEGENERATION

Xizhou Cecily Zhang[1], L. Antonschmidt[1], V. Sant[1], M. Kim[1], B. Frieg[2], D. Matthes[3], Siegfried Weisenburger[4], A. Leonov[1], S. Ryazanov[1], A. Giese[5], Vahid Sandoghdar[4], G. Unden[6], S. Becker[1], B. de Groot[3], G. Schröder[2], L. B. Andreas[1], C. Griesinger[1,7]

[1]NMR-based Structural Biology, Max-Planck-Institute for Multidisciplinary Sciences, Am Faßberg 11, Göttingen, Germany; [2]Institute of Biological Information Processing (IBI-7: Structural Biochemistry), Forschungszentrum Jülich; Jülich, Germany; [3]Department of Theoretical and Computational Biophysics, Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany; [4]Department Nano-Optics, Plasmonics and Biophotonics, Max Planck Institute for the Science of Light, Erlangen, Germany; [5]Center for Neuropathology and Prion Research, Ludwig-Maximilians-University Munich, Munich, Germany; [6]Institute for Microbiology and Wine Research, Johannes Gutenberg University of Mainz; 55128 Mainz, Germany [7]Cluster of Excellence "Multiscale Bioimaging: From Molecular Machines to Networks of Excitable Cells" (MBExC), University of Göttingen, Göttingen, Germany;

*cigr@mpinat.mpg.de

The switching of the two component system sensor CitA is effected by citrate. Transmembrane signaling due to citrate binding will be discussed (1). Further, we have studied the process of aggregation of α-synuclein on membranes *in vitro* and identified key time points in the aggregation process, that enable targeted isolation of a so called intermediate I and the fibrillar endpoint (2). Intermediate I has the characteristics of a toxic oligomer. In addition, we determined the structure of anle138b, a clinical drug candidate (3) bound to fibrils that were grown in the presence of lipids (4) that are doped with anle138b (5). Comparison of the binding site of anle138b with compounds that bind even tighter to α-synuclein fibrils and might therefore be useful for diagnostics will be discussed.

References

1) M. Salvi, B. Schomburg, K. Giller, S. Graf, G. Unden, S. Becker, A. Lange, C. Griesinger, Proc. Natl. Acad. Sci. USA 114 3115-3120 (2017); S. Weisenburger, D. Boening, B. Schomburg, K. Giller, S. Becker; C. Griesinger, V. Sandoghdar. Nat. Method. 14, 141-4 (2017); X. C. Zhang, K. Xue, M. Salvi, K. Giller, M. Stopp, S. Weisenburger, V. Sandoghdar, G. Unden, S. Becker, L.B. Andreas, C. Griesinger. doi: https://doi.org/10.1101/2023.02.06.527302

2) L. Antonschmidt, R. Dervişoğlu, V. Sant, K. A. Tekwani Movellan, I. Mey, D. Riedel, C. Steinem, S. Becker, L. B. Andreas, C. Griesinger., Sci. Adv. 7(20) eabg2174

3) J. Wagner, S. Ryazanov, A. Leonov, J. Levin, S. Shi, F. Schmidt, C. Prix, F. Pan-Montojo, U. Bertsch, G. Mitteregger-Kretzschmar, M. Geissen, M. Eiden, F. Leidel, T. Hirschberger, A. A. Deeg, J. J. Krauth, W. Zinth, P. Tavan, J. Pilger, M. Zweckstetter, T. Frank, M. Bähr, J. H. Weishaupt, M. Uhr, H. Urlaub, U. Teichmann, M. Samwer, K. Bötzel, M. Groschup, H. Kretzschmar, C. Griesinger, A. Giese, Acta Neuropathol. 125, 795-813 (2013); M. Wegrzynowicz, D. Bar-On, Calò, O. Anichtchik, M. Iovino, J. Xia, S. Ryazanov, A. Leonov, A. Giese, J. Dalley, C. Griesinger, U. Ashery, M.G. Spillantini. Acta Neuropathol. 138, 575-595 (2019); J. Levin, N. Sing, S. Melbourne, A. Morgan, M. G. Spillantini, M. Wegrzynowicz, J. W. Dalley, S. Ryazanov, A. Leonov, C. Griesinger, F. Schmidt, D. Weckbecker, K. Prager, T. Matthias, A. Giese, EBioMedicine 80, 104021 (2022); NCT04685265

4) B. Frieg, L. Antonschmidt, C. Dienemann, J. A. Geraets, D. Matthes, B. de Groot, S. Becker, L.B. Andreas, C. Griesinger, G.F. Schröder. Nat. Commun. 13, 6810 (2022)

5) L. Antonschmidt, R. Dervişoğlu, D. Matthes, C. Dienemann, A. Leonov, V. Sant, S. Ryazanov, S. Becker, A. Giese, G. Schröder, B. de Groot, C. Griesinger, L. B. Andreas. Nat. Commun. (2022) 13:5385

PL2

MULTIANALYTICAL APPROACHES FOR THE STUDY AND CONSERVATION OF CULTURAL HERITAGE - THE HERCULES LAB EXPERIENCE

António Candeias[1,2*]

[1]City University Macau Chair in Sustainable Heritage, HERCULES Laboratory and IN2PAST Laboratory, Universidade de Évora, Évora, Portugal; [2]Sino-Portugal Joint Laboratory of Cultural Heritage Conservation Science, Universidade de Évora, Évora, Portugal
*candeias@uevora.pt

The range of analytical instrumentation currently available for heritage research and conservation is broad and encompasses both *in-situ* non-invasive techniques and micro-analytical and high resolution laboratory techniques. Since each technique gives its own type of information and has its own suitability strengths and weaknesses, a previous assessment is essential to avoid a disoriented and useless examination.

One of the problems is the use of a limited analytical methodology or tendency to focus on specific research details that result in incomplete information that can be problematic for carrying out conservation interventions or historical studies. Furthermore, in most cases, no single analytical technique can determine the full composition and/or structure of an object and provide valuable conclusions. In most cases a compliance of the results from several complementary techniques must be employed.

On the other hand, sampling is often carried out to allow the analysis of art/heritage objects but recent advances in imaging and non-invasive point and mapping techniques are changing this situation and allowing the development of comprehensive non-invasive studies and integrated conservation projects. In this talk we will explore the use of multi-analytical methodologies and the integration of new non-invasive and imaging techniques with application in conservation and heritage science cooperative projects at HERCULES Laboratory.

Figure 1: Old Goa Revelations project (2022.10305.PTDC) field mission snapshots, Goa, January 2023

Acknowledgments

The author acknowledges the Portuguese Foundation for Science and Technology through the contracts UIDP/04449/2020 and UIDB/04449/2020 (HERCULES Laboratory) and the National Key R&D Program of China (2021YFE0200100).

INNOVATIONS, TECHNOLOGY DISRUPTIONS AND TARGET INTERVENTIONS FOR FUTURE FOOD

Charis M. Galanakis*

[1] Galanakis Laboratories, Chania, Greece; Taif University, Taif, Saudi Arabia; Food Waste Recovery Group, ISEKI Food Association, Vienna, Austria, Country.
* charismgalanakis@gmail.com

Over the last few years, the world has been facing dramatic changes due to a condensed period of multiple crises, including climate change, the COVID-19 pandemic, and the Russian–Ukrainian war. Although different, these crises share common characteristics and impacts, questioning food safety, security, and sustainability. In addition, they indicated that the current food systems are vulnerable and not resilient, needing a transformation toward future food. This transformation should be proactive concerning food safety, circular, digital, and inclusive (ensuring that all citizens are actively engaged). Internet and Communication Technologies, blockchain in the food supply chain and other Industry 4.0 applications, as well as approaches that redefine the way we consume food (e.g., lab-grown meat, plant-based alternatives of meat, and valorization of a vast range of bioresources), are the innovations with the highest potential in the era of future foods. In addition, food production modernization (e.g., by implementing emerging food processing technologies) and developing shorter and more domestic supply chains are also critical to achieving food resilience and security in the future.

References

Galanakis, C.M. (2023). The "Vertigo" of the Food Sector within the Triangle of Climate Change, the Post- Pandemic World, and the Russian-Ukrainian War. Foods, 12, 721. https://doi.org/10.3390/foods12040721

Galanakis, C.M., Rizou, M., Aldawoud, T.M.S., Ucak, I., Rowan, N.J. (2021) Innovations and Technology Disruptions in the Food Sector within the COVID-19 Pandemic and Post-lockdown Era. Trends in Food Science and Technology, 110, 193-200. https://doi.org/10.1016/j.tifs.2021.02.002

PL4

DOMESTIC SCIENCE - A HISTORICAL CURIOSITY IN CHEMISTRY EDUCATION?

João Paulo André,[1*]

[1] Centro/Departamento de Química da Universidade do Minho
* jandre@quimica.uminho.pt

“Domestic Science” or “Home Economics” was a field of education and research that, at the end of the 19th century and beginning of the 20th century, aspired to recognition as a scientific area of its own right, despite its dependence on chemistry, physics and biology.

Initially included in the curricula of female secondary education, especially in countries of the Anglo-Saxon world, it also become part of the educational offer of several colleges and universities, not always, however, without controversy. A century later, what remains of “Domestic Science”?

THE VERY LATEST IN SOLID-STATE BATTERIES: THE CONDENSED MATTER OR QUANTUM BATTERY

Maria Helena Braga,[1*]

[1] Faculdade de Engenharia da Universidade do Porto
* mbraga@fe.up.pt

Li-ion batteries are everywhere, from wearables to computers, satellites, and electric vehicles. However, Li-ion batteries suffer from safety problems, use cobalt, and cannot be used above 40°C. Conversely, solid-state batteries are much safer as they do not contain a flammable liquid as an electrolyte allowing using a Lithium negative electrode, which may increase the batteries' energy density. Solid-state batteries work better slightly above room temperature and may be used with advantages with positive electrodes such as sulfur that are much friendlier and widely available than cobalt.

In late 2014, we prepared the first family of batteries, primarily based on sodium ions but not containing any alkali metal or traditional electrode. These batteries are now called condensed matter or quantum batteries because they rely upon ferroelectricity, a quantum phenomenon. They are safe, sustainable, and energy dense. The drawbacks are the individual voltage of 1.3-1.4 V and an electrolyte's complex behavior that must be tamed.

Here I will compare technologies and elaborate on the technologies developed in my laboratory MatER

KEYNOTES

MESOPOROUS (ORGANO)SILICA NANOPARTICLES FOR DRUG DELIVERY

Xavier Cattoën,[1*] Ricardo Alvarado-Meza,[1] Philippe Trens,[2] Andrea Montero Oleas,[1,3] Sara Aldabe Bilmes[3]

[1] Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000, Grenoble, France; [2] ICGM University of Montpellier, CNRS, ENSCM, Montpellier, France; [3]INQUIMAE, CONICET and Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina.
*xavier.cattoen@neel.cnrs.fr

Mesoporous Silica Nanoparticles have known a tremendous interest for their potential application in nanomedicine. Indeed, they possess excellent features to be used as drug delivery vehicles such as a low toxicity, a good rigidity, a large pore volume enabling the encapsulation of large amounts of drugs, and the possibility to functionalize easily their surface, for example for targeting cancer cells [1].

However, the mechanism of their synthesis is still not completely understood, and an important variability in the NPs size and shape is observed between reported syntheses. Furthermore, whereas important research has been devoted to small pores, pure silica nanoparticles, little has been done on large-pores variants and on organosilica-based nanoparticles.

In this presentation, we will discuss some simple mechanistic investigations on the synthesis of mesoporous nanoparticles using pH monitoring and light scattering measurements [1]. We will then describe the preparation of periodic mesoporous organosilica nanoparticles, which possess very interesting adsorption properties for small molecules [2]. Finally, we will present the synthesis of original Au@mSiO_2 core-shell nanoparticles with large pores, able to encapsulate proteins such as BSA, RFP and HRP (**Figure 1**).

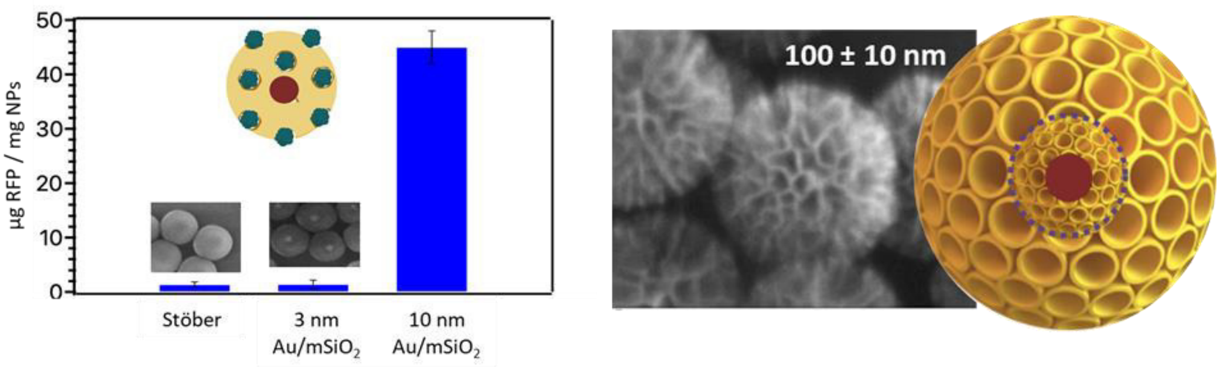


Figure 1: Encapsulation efficiency of a red fluorescent protein in dense (Stöber), small-pores or large-pores Au@mSiO_2 nanoparticles and SEM image of large-pores Au@mSiO_2 nanoparticles.

References

[1] Castillo RR, Lozano D, González B, Manzano M, Izquierdo-Barba I, Vallet-Regí M. Expert Opin Drug Deliv. 16 (2019) 415.
[2] R. Avarado-Meza, T. Santori, X. Cattoën, J. Sol-Gel Sci. Technol., *submitted*
[3] J. Croissant, X. Cattoën, M. Wong Chi Man, A. Gallud, L. Raehm, P. Trens, M. Maynadier, J.-O. Durand, Adv. Mater. 20 (2014), 6174.

Acknowledgments

The Agence Nationale de la Recherche is greatfully acknowledged for financial support (ANR-20-CE09-0017-03).

KN2

OMBINING MULTI-LEVEL BIOMOLECULAR SIMULATIONS WITH EXPERIMENTAL DATA FOR DRUG DISCOVERY

Sérgio F. Sousa

UCIBIO@REQUIMTE – BioSIM, Departamento de Biomedicina, Faculdade de Medicina da Universidade do Porto, Portugal.
*sergiofsousa@med.up.pt

Biomolecular simulations are a today an increasingly present reality in the study of how our organism functions. Based on laws of physics and taking advantage of computers they enable the behavior of biomolecules such as proteins, enzymes, and nucleic acids to be simulated in conditions that try to mimic those of the cell or the human body, yielding important clues for the development of new drugs, for the understanding of the reaction and recognition mechanisms taking place in the human body. In some cases, these simulations can go to the atomic or electronic level. The age of information has made available an increasingly amount of data that can be used to build and improve these simulations, allowing the rationalization and prediction of reality to an extraordinary level of detail, encompassing also, in some cases, the particularities of different individuals at the genomic and proteomic level.

In this talk, recently published examples on the application of biomolecular simulations in drug discovery [1,2] and in the study of molecular recognition [3,4] will be presented. These will be used to illustrate the high potential arising from the recent technological developments in the field and the opportunities brought. Examples will include the application of virtual screening, molecular dynamics simulations and free energy calculations, in close connection between with the more traditional experimental methodologies.

References

[1] Lapaillerie D et al. Antimicrobial Agents and Chemotherapy, 66 (2022) 8.
[2] Fernandes S et al. Food Research International, 165 (2023)
[3] Pereira AC et al. Molecular Systems Design and Engineering, 7 (2022), 637
[3] Santos-Pereira C et al. International Journal of Biological Macromolecules, 186 (2021), 54

Acknowledgments

This research was supported by national funds from the Portuguese Foundation for Science and Technology (FCT) under the scope of the strategic funding UIDB/04378/2020. The author acknowledges FCT by funding 2020.01423.CEECIND/CP1596/CT0003.

KN3

FROM NATURE TO PRODUCTS: NATURAL FOOD INGREDIENTS APPLICATIONS

Lillian Barros

Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
*lillian@ipb.pt

In the last decades, the study of natural ingredients of edible matrices has increased exponentially, driven by the discovery of scientific evidence that validates the wide diversity of applications and benefits arising from their utilization. Hence, the use of plants and mushrooms to improve health epitomizes a substantial cultural legacy, these been conventionally used as a basis of highly nutritional foods and medicinal preparations. Besides their nutritional richness, mushrooms and plants are known to perform various pharmacological purposes, holding a wide variety of high-value natural ingredients for several industries, acting as colorants, preservatives, and conferring bioactive properties when added to other products [1,2].

Currently, the optimization of extraction systems to increase the purity of target compounds and the respective extraction yields through innovative techniques, such as heat-assisted extractions, microwaves, ultrasound, supercritical fluid extraction and pressure system extraction, have been used to extract more promising natural molecules to be used as bio-based food ingredients/additives. These molecules include anthocyanins, betacyanins, catechins, micosterols, tannins, rosmarinic acid, among others, which have already been studied regarding their stability and cytotoxicity, and microencapsulation techniques developed, allowing their application in different food matrices [3,4], as is the case of a preservative ingredient rich in phenolic compounds incorporated into cream cheese, yogurt and biscuits, an extract rich in rosmarinic acid and chicory of basil incorporated into cheese, purple globe amaranth betacyanins in cookies, and anthocyanins in macarons. Additionally, the polyphenolic extracts of *Melissa officinalis* L. (lemon balm) and *Castanea sativa* Mill. flowers (sweet chestnut) have been showed to exert a good antioxidant and antimicrobial activities, while *Foeniculum vulgare* Mill. (fennel), and *Matricaria chamomilla* L. (german chamomile) were used for preservative purposes in loaf bread, cupcakes, yogurt, cheese, wine, and cottage cheese. On the other hand, mushrooms have also been fully exploited regarding their composition in ergosterol, which has been successfully extracted and converted into vitamin D2 to be used in functionalized dairy beverages, cheese, and flours.

Together, these results highpoint the effectiveness of natural ingredients of different mushrooms and plant species, endorsing the valorisation of these products as a source of naturally based ingredients able to be incorporated into broadly consumed and appreciated food products at an industrial/commercial level.

References [List references cited in text as]
[1] Heleno, S. Ferreira, I. Ćirić, A., et al. Food & Funsction, 5(10) (2014) 2521.
[2] Taofiq, O. Calhelha, R. Heleno, S., et al. Food Research International, 76 (2015) 821.
[3] Ribeiro, A. Caleja, C. Barros, L., et al. Food & Function, 7(5) (2016) 2185.
[4] Roriz, C. Heleno, S. Carocho, M., et al. Food Chemistry, 329 (2020) 127178.

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), and for L. Barros contract through the institutional scientific employment program-contract.

CORROSION – MATERIALS AND ENVIRONMENT

João Salvador Fernandes[1,2]

[1]Department of Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais 1049-001 Lisboa, Portugal
[2]CQE – Centro de Química Estrutural, Av. Rovisco Pais 1049-001 Lisboa, Portugal
*joao.salvador@tecnico.ulisboa.pt

Corrosion is a natural process that has been causing significant damage to materials and structures for centuries. It results from chemical or electrochemical reactions that occur between a material and its environment, leading to the gradual deterioration and weakening of the material.

The impacts of corrosion can be severe, ranging from reduced structural integrity and decreased performance to catastrophic failures that can cause injury or loss of life. Additionally, corrosion can have significant economic impacts, resulting in costly repairs, maintenance, and replacement of affected materials and equipment.

To combat corrosion, a range of anti-corrosion procedures and techniques are available. These include the use of protective coatings and inhibitors, cathodic or anodic protection, and design and material selection strategies. The effectiveness of these techniques depends on the specific circumstances of the corrosion and the materials involved.

This presentation will provide a comprehensive overview of corrosion and its impacts, as well as the work done in the Corrosion Science and Surface Engineering Group (CSSE) to address corrosion issues and to develop new products with enhanced corrosion resistance, in different fields, from the biomedical implants to corrosion sensors for aeronautics.

Acknowledgments
Thanks to all the colleagues, researchers and students involved in the presented work.
CQE is financed by FCT through contracts UIDB/00100/2020 and UIDP/00100/2020.

KN5

LUMINESCENCE WITH PROFESSOR BURROWS. PLAYING WITH LANTHANOIDS AND CONJUGATED POLYELECTROLYTES

M. J. Tapia[1]

[1]Chemistry Department, University of Burgos, Plaza Misael Bañuelos, s/n, 09901. Burgos, Spain
*mjtapia@ubu.es

In the year Professor Hugh D. Burrows has passed away, I would like to pay a heartfelt tribute to him, a scientist with a privileged mind and a brilliant academic trajectory, by overviewing some luminescent results we obtained during our long-term collaboration, mainly focused on the luminescence of trivalent lanthanoid ions and conjugated polymers interacting with surfactants, polyelectrolytes or liposomes.

The interactions of cations with anionic surfactants or polyelectrolytes are of practical and theoretical interest, *e.g.* to form metal-organic gel sensor. Trivalent lanthanoids are good models for Ca(II) with the advantage of showing well-defined luminescence properties. Eu(III) and Tb(III) lifetimes provide a direct measure of the number of coordinated water molecules through the isotope effect of replacing OH oscillators by the OD ones what causes the vibronic deexcitation pathway to become inefficient. [1] Lanthanoid complexation with sodium dodecyl sulfate (SDS) or sodium poly(vinyl sulfonate) (PVS), leads to the loss of one to six hydration water molecules, respectively. [2] In addition, Ce(III) has a reasonable molar absorption coefficient and has been shown to be capable of transferring its electronic energy to other lanthanoids such as Eu(III) and Tb(III) what requires a close contact favored by binding or complexation with micelles of polyelectrolytes. [2]

On the other hand, conjugated polyelectrolytes (CPEs), that combine the luminescence properties of conjugated polymers and the solubility of polyelectrolytes in water or polar solvents, are important materials with applications in areas such as charge transport layers in optoelectronic devices, optical sensors and biomedical imaging agents. [3] However, the fairly rigid fluorene-based CPEs tend to aggregate, which leads to low solubility, a marked decrease in the photoluminescence quantum yields and slight red shift in emission. One successful strategy to increase the photoluminescence quantum efficiencies of CPE is complexation with surfactants. At concentrations above their critical micelle concentrations (*cmc*) the neutral surfactant n-dodecyl pentaoxyethylene glycol ether ($C_{12}E_5$) causes significant increases in the emission quantum yield of sodium poly{9,9-bis[(4-butylsulfonate)phenoxy]-2,7-fluorene-alt-1,4-phenylene} (PBS-PFP), what is explained by the surfactant-induced break-up of polymer aggregates and the incorporation of single polymer chain in elongated $C_{12}E_5$ micelles. [4] Similar behaviours have been observed in other systems suggesting that the CPEs optical properties can be modulated through the interactions with surfactants. Additionally, the intercalation of the neutral poly(9,9-dioctylfluorene), PFO, into the phospholipid bilayer of 1,2-dimyristoyl-*sn*-*glycero*-3-phosphatidylcholine (DMPC) liposomes, leads to fluorescent nanoparticles in solution with PFO β-phase formation characterized by an enhanced and well resolved fluorescence. [5]

References

[1] W. D. Horrocks, D. R. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.
[2] M. J. Tapia, H. D. Burrows, Langmuir 18 (2002) 1872.
[3] B. Liu; G. C. Bazan, in Conjugated Polyelectrolytes, Chichester, John Wiley & Sons, 2012.
[4] H. D. Burrows, M. J. Tapia, S. M. Fonseca, S. Pradhan, U. Scherf, C. L. Silva, A. A. C. C. Pais, A. J. M. Valente, K. Schillén, V. Alfredsson, A. M. Carnerup, M,. Tomsic, A. Jammnik, Langmuir 25 (2009) 5545.
[5] M. J. Tapia, M. Monteserín, H. D. Burrows, J. A. S. Almeida, A.A.C.C. Pais, J. Pina, J. S. Seixas de Melo, S. Jarmelo, J. Estelrich, Soft Matter, (2015) 303.

Acknowledgments

MEC, FEDER and Burgos University are thanked for financial support through the projects *MAT2004-03827* and MAT2008-06079/MAT.

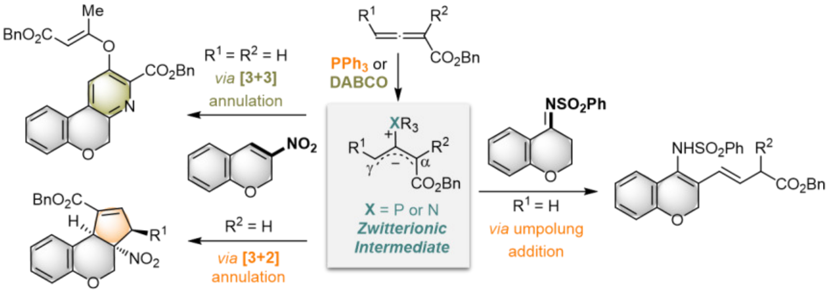
INVITED LECTURES

GENERATION OF MOLECULAR DIVERSITY VIA LEWIS BASE-CATALYZED REACTIONS OF CHROMANE SCAFFOLDS AND ALLENOATES

Maria I. L. Soares,* Teresa M. V. D. Pinho e Melo

University of Coimbra, Coimbra Chemistry Centre (CQC) – Institute of Molecular Sciences and Department of Chemistry,
3004-535 Coimbra, Portugal.
*misoares@ci.uc.pt

Allenic esters (allenoates) are attractive building blocks in organic synthesis owing to their straightforward preparation and diverse reactivity that can be modulated by selection of the appropriate Lewis base (LB) catalyst [1]. In the reaction with electrophiles, namely activated alkenes and imines, the zwitterionic intermediate generated by addition of a LB to the allenoate's β-carbon reacts differently depending on the nature of the LB. Under phosphine catalysis [3+2] annulation products are obtained, whereas in the presence of tertiary amines, conjugate additions are observed. On the other hand, allenoates react with nucleophiles to give Michael-type adducts. However, umpolung addition is observed in the presence of a catalytic amount of a phosphine affording γ-adducts.
Our group has been focused on the LB-catalyzed reactions of allenoates and the chromane scaffold as an approach for the construction of structurally diverse chromane-based frameworks, systems that are frequently found at the core of a wide variety of natural products and synthetic analogues with remarkable biological activities [2]. Fused-chromano systems were obtained *via* PPh_3- or DABCO-catalyzed [3+2] or [3+3] annulation reactions of allenoates and 3-nitro-2*H*-chromenes, respectively [3,4], while substituted 2*H*-chromenes were obtained by phosphine-catalyzed umpolung γ-addition of chroman-4-imines to allenoates (**Scheme 1**). Herein, our latest studies on the LB-catalyzed reactions of allenoates and chromane derivatives bearing activated alkene or imine functionalities will be presented.



Scheme 1: LB-catalyzed reactions of 3-nitro-2*H*-chromenes and chroman-4-imines with allenoates

References
[1] a) S. Ma, *Aldrichim. Acta*, 40 (2007) 91; b) T. M. V. D. Pinho e Melo, *Monatsh. Chem.*, 142 (2011) 681.
[2] a) S. A. Patil, R. Patil, L. M. Pfeffer, D. D. Miller, *Fut. Med. Chem.*, 5 (2013) 1647; b) R. Pratap, V. J. Ram, *Chem. Rev.*, 114 (2014) 10476; c) M. Costa, T. A. Dias, A. Brito, F. Proença, *Eur. J. Org. Chem.*, 123 (2016) 487; d) H. C. Shen, *Tetrahedron*, 65 (2009) 3931.
[3] M. I. L. Soares, C. S. B. Gomes, S. C. C. Nunes, A. A. C. C. Pais, T. M. V. D. Pinho e Melo, *Eur. J. Org. Chem.* (2019) 5441.
[4] M. I. L. Soares, C. S. B. Gomes, M. C. Oliveira, J. Marçalo, T. M. V. D. Pinho e Melo, *Org. Biom. Chem.*, 19 (2021) 9711.

Acknowledgments
Thanks are due to Coimbra Chemistry Centre (CQC), supported by the Portuguese Agency for Scientific Research "Fundação para a Ciência e a Tecnologia" (FCT), through project UIDB/00313/2020 and UIDP/00313/2020, co-funded by COMPETE2020-UE. The authors also acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt)

EXPLOITING THE CHEMICAL MODIFICATIONS OF LAMINARIN TO DEVELOP TUNABLE BIOMATERIALS FOR BIOMEDICAL APPLICATIONS

João M.M. Rodrigues,[1*] Luís P. Monteiro,[1] Edgar Castanheira,[1] Margarida A. Sacramento,[1] João F. Mano[1]

[1]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal.
*jrodrigues@ua.pt

The marine environment is an extraordinary source of marine living resources of natural molecules and materials with specific biological and chemical features that can be readily extracted from. Among them, marine-origin biopolymers find widespread use in a wide array of biomedical applications [1]. Moreover, the marine environment also encompasses invertebrate organisms glued to wet surfaces due to particularly adhesives. These adhesives are secreted by marine sessile organisms, such as mussels, barnacles, and sandcastle worms, and adhere effectively and strongly to almost any underwater surface [2]. Through the combination of the active biomolecules present in these organisms and the use of marine polysaccharides due their biological and physicochemical properties, including **a)** biocompatibility, **b)** biodegradability, and **c)** versatility in modification, is possible to develop advanced biomaterials for biomedical applications [1,2]. Here, straightforward and selective chemical methodologies to be applied in Laminarin (LAM), [3-5] a natural origin polysaccharide from brown algae, modifying its chemical backbone structure, for further conjugation with different small molecules, such as active –functional or –catechol groups (Figure 1), will be presented. Novel derivatives were prepared and used to produce several LAM-based biomaterials with potential for tissue regeneration purposes. Several chemical modification steps for the insertion of functional groups, such as –allyl, –alkyl, –azide, –methacroyl and –catechol groups, are reported and the final properties of the develop biomaterials (microparticles, hydrogels, cryogels and thin films) will be discussed.

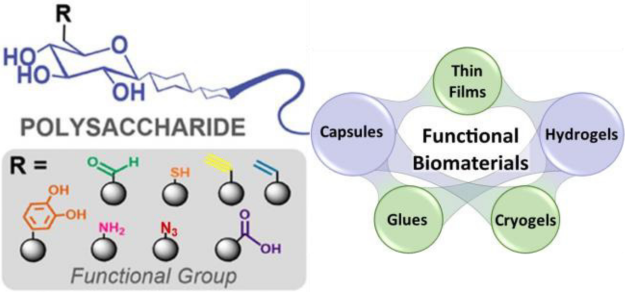


Figure 1: Chemical modifications of LAM polysaccharide

References

[1] M.M.A. Sacramento, J. Borges, F.J.S. Correia, R. Calado, J.M.M. Rodrigues, S.G. Patrício, J.F. Mano, *Front. Bioeng. Biotechnol.*, 10 (2022) 1041102.
[2] W. Zhang, R. Wang, Z.M. Sun, X. Zhu, Q. Zhao, T. Zhang, A. Cholewinski, F.K. Yang, B. Zhao, R. Pinnaratip, P.K. Forooshani, B.P. Lee, *Chem. Soc. Rev.*, 49 (2020) 433.
[3] E.J. Castanheira, T.R. Correia, J.M.M. Rodrigues, J.F. Mano, *Bull. Chem. Soc. Jpn.,* 93 (2020) 713.
[4] A.M.S. Costa, J.M.M. Rodrigues, M.M. Pérez-Madrigal, A.P. Dove, J.F. Mano, *J. Am. Chem. Soc.,* 142 (2020) 19689.
[5] L.P.G. Monteiro, J. Borges, J.M.M. Rodrigues, J.F. Mano, *Mar. Drugs,* 21 (2023) 92.

Acknowledgments

Thanks are due to Fundação para a Ciência e a Tecnologia (FCT) for funding CICECO research unit (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020). This research was funded by the Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (OE) through FCT/MCTES in the scope of the project COP2P (PTDC/QUIQOR/30771/2017 – POCI-01-0145-FEDER-30771). L.P.M., E.C., M.AS and J.M.M.R. gratefully acknowledge FCT for the individual PhD grants (2020.06767.BD – L.P.G.M.; SFRH/BD/144880/2019 – E.C.; 2020.07156.BD – MAS) and individual researcher contract (CEECIND/01363/2018 – J.M.M.R.), respectively.

IL3

STRATEGIES TO ADDRESS HARD-TO-ACCESS BRAIN TUMORS USING SOLID LIPID NANOPARTICLES

Maria Mendes[1,2], João Basso[1,2], José Sereno[3,4], Maria António[5], Ana L. Daniel-da-Silva[5], Tânia Cova[2], Sandra Nunes[2], Maria Luísa Ramos[2], Ana Fortuna[1,3], Miguel Castelo-Branco[3,4], Amílcar Falcão[1,3], João Sousa[1,2], Alberto Pais[2], Carla Vitorino[1,2]

[1]1Faculty of Pharmacy, University of Coimbra, Coimbra, Portugal; [2]Coimbra Chemistry Centre, Institute of Molecular Sciences - IMS, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal; [3]Coimbra Institute for Biomedical Imaging and Translational Research (CIBIT), University of Coimbra, 3000-548 Coimbra, Portugal; [4]Institute of Nuclear Sciences Applied to Health (ICNAS), University of Coimbra, 3000-548 Coimbra, Portugal; [5]CICECO-Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193, Aveiro, Portugal;
*csvitorino@ff.uc.pt

We have hypothesized that ultra-small nanostructured lipid carriers (usNLCs), a particular type of solid lipid nanoparticles, can enhance site-specific drug delivery, especially in the case of glioblastoma (GB), the most deadly type of brain tumor.

One of our approaches has been directed to the development of a surface-conjugated usNLC prototype for multi-target delivery against tumor cells and the surrounding microenvironment. Atorvastatin and curcumin were tested as complementary therapies and their co-encapsulation was studied for its colloidal properties, stability, and release behavior. The effects of usNLC modification with hyaluronic acid conjugates, peptides cRGDfK and H7k(R2)2, and folic acid on GB cells were examined for cytotoxicity, internalization, uptake mechanism, and hemolytic character. The usNLCs were found to have favorable biodistribution, tolerability, and efficacy in GB-bearing mice through magnetic resonance imaging and spectroscopy. The modified usNLCs showed improved targeting to the brain and reduced elimination by clearance organs. Tumor growth was inhibited in mice treated with the usNLCs, while unencapsulated therapeutic agents caused tumor growth to exceed 181% over the same period.

In another approach, we developed hybrid nanoparticles (HNPs) to enhance current therapies by combining chemical and physical strategies. The HNPs were constructed by linking usNLCs (organic moeiety) and gold nanorods (inorganic moeiety) and directed towards the blood-brain barrier using transferrin as an active targeting. Results showed higher cytotoxicity and uptake in glioblastoma cells compared to non-targeted nanoparticles, with preferential accumulation in the brain and higher mean residence time. In vivo experiments in a human glioblastoma orthotopic model showed significantly enhanced antitumor ability with 4.10-fold inhibition of tumor volume, longer lifespan of animals, and better tolerability compared to TMZ.

Overall, these results suggest that surface modification is a promising approach to enhance lipid nanoparticle performance and offer new strategies for GB, a pressing medical need.

TOWARDS A GREENER PHARMACEUTICAL INDUSTRY. THIS IS THE WAY!

Mafalda 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 CO2 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 talk, 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 talk is to show greener roots for the pharmaceutical (and not only) industry to employ for an environmental safer and sustainable industry.

References

[1] [Belkhir, L.; Elmeligi, A., Journal of Cleaner Production, 214 (2018) 185.
[2] Pacheco-Fernández I, Pino V., Current Opinion in Green and Sustainable Chemistry, 18 (2019) 42.
[3] Rogers L, Jensen KF., Green Chemistry, 21 (2019) 3481.
[4] Beaver MG, Caille S, Içten E, Michalak SE, St-Pierre G, Thiel OR., Israel Journal of Chemistry. 61 (2021) 369.
[5] Clark JH, Green Chemistry, 8 (2006) 17.
[6] Silvestri C, Silvestri L, Forcina A, Di Bona G, Falcone D., Journal of Cleaner Production, 294 (2021) 126137.

Acknowledgments

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. Mafalda Sarraguça thank FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória.

IL5

TURNING WASTEWATERS INTO A VALUABLE RESOURCE

Leonor C. Ferreira

Associação Fraunhofer Portugal Research – AWAM, Regia Douro Park, Andrães, 5000-033 Vila Real, Portugal
*leonor.ferreira@awam.fraunhofer.pt

Water scarcity is a worldwide reality, therefore, mitigation strategies are being investigated and adopted to preserve this precious resource. Being a highly water-dependant sector, agriculture is expected to be strongly impacted. According to OECD, agricultural irrigation alone accounts for accounts for 70% of all the freshwater abstracted, and moreover, 80% of all generated wastewater is released without a proper treatment. In this line, wastewaters are now seen as a valuable resource and its reuse is being implemented globally [1].

Nowadays, several industries have already established a wastewater treatment plant inside their facilities but usually, the goal is to treat the wastewater in order to comply with the regulations for discharging into the municipal wastewater treatment plant or into the environment. In fact, these secondary treatment is able to reduce the content in organic matter but is not efficient in the removal of recalcitrant compounds, such as contaminants of emerging concern. Furthermore, the presence of pathogenic microorganisms hinders its direct reuse.

To this end, a tertiary wastewater treatment envisaging process technologies for water recover is crucial but at the same time challenging. These process technologies encompass Advanced Oxidation Processes (AOPs), membrane-based solutions and sensors for in-line detection. Water reuse policies demand high-quality treated water, ensuring no harm to human health or ecosystems [2-5].

This lecture will address several AOPs, membrane-based solutions, and an online monitoring device as technological tools to attain the requirements for water reuse.

The application of scientific knowledge into technological development and innovation is essential, not only to meet the stakeholders' demands but also to reach a possible and sustainable future.

References

[1] R. Simhayov, N. Ohana-Levi, M. Shenker, Y. Netzer, Agric. Water Manag., 275 (2023) 108002.
[2] L.C. Ferreira, M. Castro-Alférez, S. Nahim-Granados, M.I. Polo-López, M.S. Lucas, G. Li Puma, P. Fernández-Ibáñez, Chem. Eng. Journal, 381 (2020) 122275.
[3] L.C. Ferreira, I. Salmerón, J.A. Peres, P.B. Tavares, M.S. Lucas, S. Malato, Water Resour. Ind., 24 (2020) 100137.
[4] N. Steinke, M. Rio, R. Wuchrer, C. Schuster, E. Ljasenko, D. Knopp, G. Gerlach, T. Härtling, Sens. Actuators B Chem., 254 (2018) 749-754,
[5] L.C. Ferreira, J.R. Fernandes, J.A. Peres, P.B. Tavares, M.S. Lucas, Environ. Res., 200 (2021) 111430

Acknowledgments

Author is grateful to the Project INICIO - Setup of research infrastructure for closed circles of water, nutrients and energy in Portuguese agriculture (NORTE-01-0145-FEDER-072685).

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

ARE MELON BY-PRODUCTS A SUITABLE SOURCE OF NUTRIENTS AND BIOACTIVE COMPOUNDS FOR THE DEVELOPMENT OF FUNCTIONAL FOODS?

Tânia Gonçalves Albuquerque,[1,2*] Mafalda Alexandra Silva,[1,2] M. Beatriz P.P. Oliveira,[2] Helena S. Costa[1,2]

[1]Department of Food and Nutrition, National Institute of Health Dr. Ricardo Jorge, I.P., Lisbon, Portugal; [2]REQUIMTE-LAQV/Faculty of Pharmacy, University of Oporto, Oporto, Portugal.
*tania.albuquerque@insa.min-saude.pt

Introduction: Today's consumers are demanding for foods which not only have enhanced nutritional profile but also have health benefits, known as functional foods. By-products of the food and agricultural industries, such as peels and seeds of fruits, have been found to have additional uses, thereby solving waste problems, reducing environmental impacts, and increasing their commercial value. It is expected that the generated amounts of by-products will continue to significantly increase and the application of such by-products, as ingredients, for the development of functional foods will be, for sure, an excellent opportunity to valorise this waste and to promote sustainability.

Aim: To valorise melon by-products, by using a sustainable approach, to further develop enriched and nutritional balanced functional foods (with low saturated fat, salt, and sugar content) that will contribute to the improvement of various public health challenges (type 2 diabetes, obesity, cardiovascular diseases, and hypertension).

Material and methods: In 2022, melon by-products (seeds and peels) were collected directly from Portuguese producers. The melon peels were dehydrated (50 ºC, 10h) and the seeds were dried in an oven (50 ºC, 6h). Afterwards, samples were grinded to obtain melon peel flour (MPF) and melon seeds flour (MSF). The following components were analyzed: moisture, ash, protein, amino acids, fat, fatty acids, dietary fiber and vitamins. Then, a holistic approach considering the overall nutritional profile of the flours was performed to establish the best methodology for the design of healthy functional foods. Results are presented per 100 g of dry weight (dw).

Results: The main component of both flours is dietary fiber (30.5 ± 0.4 and 42.3 ± 2.3 g/100 g dw for MSF and MPF, respectively). The MSF presented a higher content of protein (22.8 ± 0.7 g/100 g dw) and of total fat (30.5 ± 0.4 g/100 g dw), in comparison with MPF. Regarding vitamin E, the main vitamers for both flours were γ-tocopherol and α-tocopherol. According to nutrition claims, Regulation (EC) n.º 1924/2006, MSF is high in fiber, while MPF is high in fiber and low in fat. The dietary reference value for vitamin E intake, for adults, is 11 mg/day and 13 mg/day, for female and male, respectively. The analyzed flours can be considered a good source of this vitamin to accomplish the dietary recommendations.

Conclusions: Melon by-products are a valuable source of nutrients and bioactive compounds and this research contributes with scientific knowledge for the design of multi-functional ingredients, which can be further used to develop nutritious and healthy functional foods. These by-products have potential to globally improve food security, nutrition, and economic well-being.

Acknowledgments

This work was financially supported by Foundation for Science and Technology (FCT) under the projects Food4DIAB (EXPL/BAA-AGR/1382/2021); and UIDB/50006/2020 and by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) co-financed by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020).

WORKSHOP

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

CRASH COURSE ON OPEN SCIENCE AND DATA

Pedro S. F. Mendes

Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal
*pedro.f.mendes@tecnico.ulisboa.pt

The history of chemistry is a story of open science. Only by decades and centuries of data sharing and curation, namely of the experiments measuring the properties of the various chemical elements, Mendeleev was able to put together the Periodic Table. However, today chemistry is lagging behind in terms of open science practices. For both chemical sciences and chemical engineering, data sharing is significantly lower as compared to contiguous fields [1]. At the same time, the services and resources currently provided at the European level (by EOSC) to support researchers in sharing their data are also scarce (e.g. 4 times less for chemistry than biology, 11 times less for chemical engineering than environmental engineering).

The goal of open science is to break the barriers of knowledge. In particular, promoting data recycling and reuse via data sharing (Fig. 1).

In this "Crash course on open science and data", you will get know the of (i) why open science is important, (ii) what is data management about, and (iii) the very basics of how and where you can share your data. You will learn how to share data openly and get ready to publish your first dataset. You will bring a dataset (can be a published one, any technique/software) and we will work on it to get it ready to share in way useful both to you and your community.

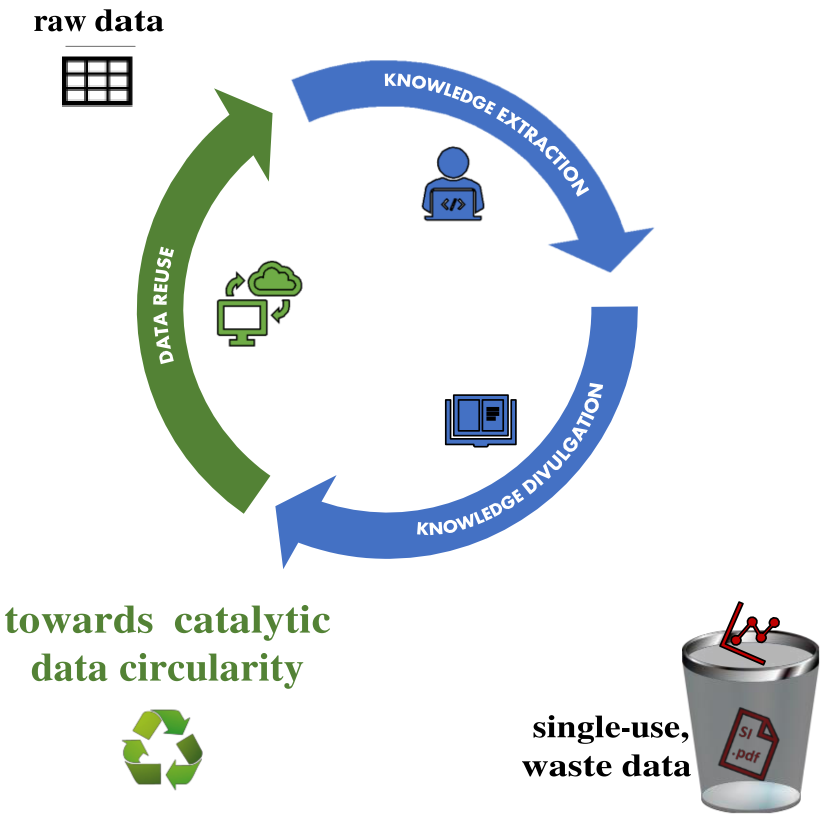


Figure 1: Scientific data cycle, highlighting data reuse (adapted from [1]).

References

[1] P.S.F. Mendes, S. Siradze, L. Pirro, J.W. Thybaut, ChemCatChem, 13 (2021), 836-850.

Acknowledgments

Pedro S. F. Mendes acknowledges FCT funding to CQE (UIDB/00100/2020 e UIDP/00100/2020) and EU H2020 funding via EOSC Future ambassadorship (101017536).

ORAL COMMUNICATION

HIGH-PRESSURE PRE-TREATMENT TO TAILOR STARCH-BASED FILMS PROPERTIES?

Renata A. Amaral,[1] Ana P. Martins,[1,2] Carlos A. Pinto,[1] José Lopes da Silva,[1] Jorge A. Saraiva,[1*]

[1]LAQV-REQUIMTE, Chemistry department, Aveiro University, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal;
[2]CICECO, Chemistry department, Aveiro University, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal;
*jorgesaraiva@ua.pt

Thermoplastics have become an integral part of our daily lives, and although synthetic non-biodegradable polymers have several advantages, such as low prices and simple industrial processing, they pose a threat to the world's sustainability as they generate vast quantities of non-biodegradable wastes. As a result, several strategies have been utilized to develop biodegradable packaging, primarily from biodegradable biopolymers such as starch [1]. Starch is an essential biopolymer due to its renewable nature, low cost (it can be extracted from industrial byproducts), and wide availability. In addition, multiple studies have demonstrated that starch-based films and coatings are appropriate because they are odorless, colorless, provide an aesthetically pleasing appearance, can act as an antioxidant and antimicrobial carrier, and are edible [2]. Despite this, these films can present obstacles such as high hydrophilicity and degradation. Physical, chemical, and enzymatic techniques can be used to modify starch so that its properties better suit food and industrial applications [3]. Some alternative processing techniques, such as high-pressure processing, can induce substantial changes in the physical, chemical, and functional properties of starches [4]. High Pressure Processing (HPP) can be utilized because it can break or alter the non-covalent chemical bonds in starch and modify starch to achieve the desired properties, being already used to modify macromolecules, for cold starch gelatinization or protein denaturation, with the ability to affect the properties of the resulting films [5].

Considering this, the objective of this study was to investigate the effect of HPP (350 or 500 MPa for 5 or 15 minutes) as a starch pre-treatment in conjunction with a pre-gelatinization step lasting 30 or 165 minutes. The developed films were compared with the untreated ones using FTIR, XRD, TGA, DSC, SEM and in terms of mechanical properties (elongation at break, tensile strength, young's modulus), hydrophobicity, color, transparency, moisture, water solubility and water vapor permeability (WVP).

Results indicated that all films are transparent, and those treated with pressure have a smoother surface, which is more pronounced in starch-based films subjected to pressure for longer periods. Films subjected to a 350 MPa - 5 minute treatment exhibited a greater hydrophobicity and a lower WVP. On the other hand, higher elongation at break and lower tensile strength were observed for 500 and 350 MPa HP treatments. Consequently, it can be concluded that starch pre-treatments are effective for modifying starch-based films and can be used to produce films with enhanced properties.

References

[1] Nilsen-Nygaard, J., Fernández, E. N., Radusin, T., Rotabakk, B. T., Sarfraz, J., Sharmin, N., Sivertsvik, M., Sone, I., & Pettersen, M. K, Comprehensive Reviews in Food Science and Food Safety. (2021) 1-48.
[2] S. Kim, S. Yang, H. Hyun, and K. Bin, Food Hydrocolloids, 81 (2018) pp. 71–76.
[3] Li, P., He, X., Dhital, S., Zhang, B., & Huang, Q, Carbohydrate Polymers, 169 (2017) 351–356.
[4] Thomas, E., Panjagari, N. R., Singh, A. K., Sabikhi, L., Deshwal, G. K. Jorn of Food Science and Technology, 1 (2022). 1–20
[5] Castro, L. M. G., Alexandre, E. M. C., Saraiva, J. A., & Pintado, M., Food Hydrocolloids, 106 (2020) 105877

Acknowledgments

Thanks are due to the University of Aveiro and FCT/MCT for the financial support to the LAQV-REQUIMTE research Unit (UIDB/50006/2020 & UIDP/50006/2020) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement. Renata Amaral also acknowledges FCT/MCT for the PhD grant reference SFRH/BD/146009/2019

CONFINED SILVER NANOPARTICLES IN IONIC LIQUID FILMS

Alexandre C. P. M. Alves, Luís M. N. B. F. Santos, Margarida Bastos, José C. S. Costa

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto, Portugal,

* up201503618@up.pt

This work reports the formation of silver nanoparticles (AgNPs) by sputter deposition in thin films of three different ionic liquids (ILs) with the same anion (bis(trifluoromethylsulfonyl)imide) and cation (imidazolium) but different alkyl chain length of the cationic moiety ($[C_4C_1im][NTf_2]$, $[C_2C_2im][NTf_2]$ and $[C_5C_5im][NTf_2]$) [1]. Ionic liquid (IL) films in the form of microdroplets with different thicknesses (200 to 800 monolayers) were obtained through vacuum thermal evaporation onto glass substrates coated with indium tin oxide (ITO) [2,3]. The sputtering process of Ag onto ILs when conducted simultaneously with argon plasma promoted the coalescence of microdroplets of ILs and the incorporation and stabilization of AgNPs in the coalesced IL films (**Figure 1**). The formation/stabilization of AgNPs into the IL films was confirmed through high-resolution scanning electron microscopy (SEM) and UV-Vis spectroscopy. It was found that the IL films with larger thicknesses (600 and 800 monolayers) were a better media for the formation of AgNPs. Among the ILs used, $[C_5C_5im][NTf_2]$ was found to be particularly promising for the stabilization of AgNPs. When large IL droplets were exposed to argon plasma and Ag bombardment, they behaved as confining agents for the stabilization of AgNPs in IL films, thus avoiding their aggregation.

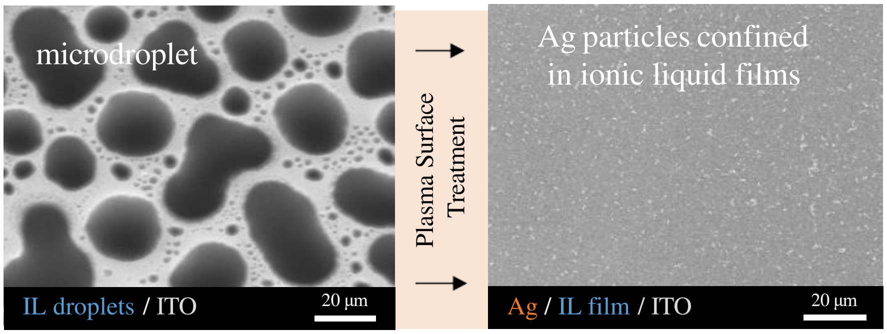


Figure 1: Morphology of micro-/nanodroplets of IL deposited by PVD on ITO (image on the left) and the respective morphology after plasma surface treatment and deposition of Ag (image on the right).

References

[1] A.C.P.M Alves.; L.M.N.B.F. Santos; M. Bastos; J.C.S. Costa, Molecules 28 (2023), 3029.

[2] R.M. Campos; A.C.P.M. Alves; M.A.L. Lima; A.F.M. Farinha; J.P.S. Cardoso; A. Mendes; J.C.S. Costa; L.M.N.B.F. Santos, ChemPhysChem, 21 (2020), 1814–1825.

[3] J.C.S. Costa; A. Alves; M. Bastos; L.M.N.B.F. Santos, Phys. Chem. Chem. Phys., 14 (2022), 13343–13355.

Acknowledgments

The authors thank the Portuguese Foundation for Science and Technology (FCT) for financial support to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020), Faculty of Science, University of Porto. A.C.P.M.A. also thanks the FCT for the award of a Ph.D. Research Grant (ref. 2022.11108.BD).

IN VITRO ANTIMICROBIAL STUDIES OF MESOPOROUS SILICA NANOPARTICLES COMPRISING ANIONIC CIPROFLOXACIN IONIC LIQUIDS AND ORGANIC SALTS

Luís Filipe,[1*] Telma de Sousa,[2] Dário Silva,[1] Miguel M. Santos,[1] Manuela Ribeiro Carrott,[3] Patricia Poeta,[2] Luis C. Branco,[1] Sandra 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]Microbiology and Antibiotic Resistance Team (MicroART), Universidade de Trás-os-Montes e Alto Douro, Departamento de Ciências Veterinárias, 5000-801 Vila Real, Portugal; [3]Centro de Química de Évora, LAQV-REQUIMTE, Universidade de Évora, Instituto de Investigação e Formação Avançada, Departamento de Química, Escola de Ciências e Tecnologia, Colégio Luís António Verney, 7000-671 Évora, 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]. Recent findings have found that mesoporous silica nanoparticles (MSNs) can be very promising nanomaterials to treat bacterial infections when combined with pharmaceutical drugs [2].

In this communication, we report a synthetic method to obtain four different sets of nanomaterials, based on the immobilization of ciprofloxacin — a member of the fluoroquinolone antibiotics family — as counter-ions of cholinium ([MSN-Chol][Cip]), pyridinium ([MSN-Pyr][Cip]), picolinium ([MSN-3-Pic][Cip]) and methylimidazolium ([MSN-1-MiM][Cip]) cations. 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 corresponding materials with the immobilized antibiotic. All materials were characterized by NMR spectroscopy, FT-IR, elemental analysis, X-ray powder diffraction and N_2 adsorption.

Antimicrobial studies were performed against sensitive and resistant strains of gram-negative *K. pneumoniae* and gram-positive *E. faecalis*. Very promising results were found for all sets of materials functionalized with the antibiotic, which outperformed free ciprofloxacin. The highest prominence was found against the antibiotic-resistant strains of *K. pneumoniae* as some materials have seen a 10-fold reduction in the minimum inhibitory concentration (MIC) comparing to free ciprofloxacin. Toxicity studies in human cell lines are currently being performed in order to validate the nanomaterials.

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, with high emphasis on the fight against bacterial resistance. Furthermore, the use of nanoparticles to treat infectious diseases can lead to formulations that are more active and fewer side effects [2].

References

[1] A. Coates, Y. Hu, R. Bax, C. Page, The future challenges facing the development of new antimicrobial drugs, Nat. Rev. Drug Discov., 1, (2002) 537.

[2] B. de Juan Mora, L. Filipe, A. Forte, M.M. Santos, C. Alves, F. Teodoro, R. Pedrosa, M. Ribeiro Carrott, L.C. Branco, S. Gago, Boosting Antimicrobial Activity of Ciprofloxacin by Functionalization of Mesoporous Silica Nanoparticles, Pharmaceutics. 13 (2021) 218

Acknowledgments

The authors thank Fundação para a Ciência e Tecnologia for the projects PTDC/QUI-QOR/32406/2017, PEst-C/LA0006/2013, RECI/BBBBQB/0230/2012 as well as MAR2020 (MAR-02.01.01-FEAMP-0042–INOVA4AQUA). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project N° 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). LF also thanks FCT (2021.08347.BD).

UNRAVELING THE MECHANISMS OF CELLULAR PERMEATION OF LUZ51

Mafalda Penetra,[1] Luís G. Arnaut ,[1] Lígia C. Gomes-da-Silva[1]

[1]CQC, Chemistry Department, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal.
Corresponding author: mafaldapenetra.p@gmail.com

Photodynamic therapy (PDT) is a promising strategy for cancer treatment. It is a highly selective and minimally invasive therapeutic procedure that relies on three components: a photosensitizer (PS), that ideally absorbs light in the phototherapeutic window (650-850 nm), and molecular oxygen to form reactive oxygen species (ROS) in the target tissues. ROS have a short life span and can only diffuse over a limited distance thereof, the PDT effect is largely dependent on the characteristics of the PS, and its distribution in tissues and organelles within the cell [1]. The interaction and permeation of therapeutic molecules across cell membranes is critical for ensuring intracellular bioavailability at therapeutic concentrations. According to the lipophilicity and size of the molecule, the mechanism by which molecules internalize cells can vary. Small molecules with relative lipophilicity tend to internalize cells through energy-independent processes that are largely regulated by the concentration gradient (e.g., passive diffusion). On the other hand, large and more hydrophilic molecules require energy-dependent processes (e.g. endocytosis) [2]. The PS under evaluation in this work was LUZ51, a relatively small and amphiphilic carboxamide bacteriochlorin (595 g/mol and log $P_{o/w}$ 2.9) [3]. The mechanisms of influx and efflux of LUZ51 were investigated by taking advantage of its intrinsic fluorescence. For that, the internalization of LUZ51 was evaluated by co-incubating 4T1 cells with inhibitors of a variety of mechanisms of cell uptake. The effect of temperature and ATP was also studied. The results show that the internalization of LUZ51 was significantly decreased at 4ºC, but not when ATP was depleted neither when inhibitors of mechanisms of active transport were used. Upon cell wash, LUZ51 was secreted to the extracellular medium. This process was not inhibited by P-glycoprotein inhibitors. Therefore, we may infer that LUZ51 is rapidly internalized by cells through passive diffusion and that its efflux is apparently independent of efflux pumps.

References

[1] J.M. Dabrowski, L.G. Arnaut, Photochem. Photobiol. Sci. 14 (2015) 1765–1780.
[2] E. Cocucci, J. Kim, Y. Bai, N. Pabla, Clin. Pharmacol. Ther. 101 (2017) 121–129.
[3] G.P.N. Costa, N.P.F. Gonçalves, C.J.P. Monteiro, A.C.R. Abreu, H.T.F.C. Soares, L.G.B. Rocha, F.A. Schaberle, M.M. Pereira, L.G. Arnaut, Low Molecular Weight Derivatives of Carboxamide Halogenated Porphyrins, Namely Chlorins and Bacteriochlorins, and Their Applications Thereof, EP 3292129, 2018.

Acknowledgments

This project has received funding from the Portuguese Foundation for Science and Technology (UID/QUI/00313/2019, PTDC/QUI-OUT/0303/2021 and EXPL/BIA-CEL/1295/2021).

NEW DEVELOPMENTS IN BIOCIDE CHEMOSENSORS: ARE QUINOLINE-BASED HYDRAZONES ANY GOOD?

Rui P. C. L. Sousa,[1*] Filipe Teixeira,[1] Susana P. G. Costa,[1] Rita B. Figueira,[1] M. Manuela M. Raposo[1]

[1] Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal
*rui.sousa@quimica.uminho.pt

Biocides, such as tributyltin (TBT), are used worldwide in the composition of paints, to mitigate biofouling on ships and vessels. However, this compound was found to cause damage to aquatic organisms, after leaching from the submerged structures in which the paint was applied [1]. Even though TBT was banned by the Rotterdam Convention, its effects are still impacting aquatic environments. Therefore, TBT monitoring is a critical task for the preservation of marine species, which is currently performed by means of expensive and time-consuming sampling and laboratory analysis [2]. Thus, devising a TBT monitoring equipment that could be used *in situ* would be of utter importance. Despite this, the development of TBT sensor devices remains quite an unexplored field.

In this work we report the synthesis of 6 new quinoline-based hydrazones (HZ), which were devised as potential TBT optical chemosensors. These new compounds were obtained by condensation reactions between formyl-quinoline precursors and different hydrazines, in yields ranging from 53 to 95 %. Three of these compounds were found to be sensitive to TBT, and spectrophotometric/spectrofluorimetric titrations were performed to analyze the interaction. The limits of detection (LOD) found were in the range of 1 to 20 µM. In order to understand why these features are only noticeable in some compounds, the structure of the HZ-TBT complexes was optimized using DFT calculations and their structural features correlated to the experimental observations. The results show that this type of compounds is promising to be applied as TBT transducers in the construction of an *in situ* TBT sensory device.

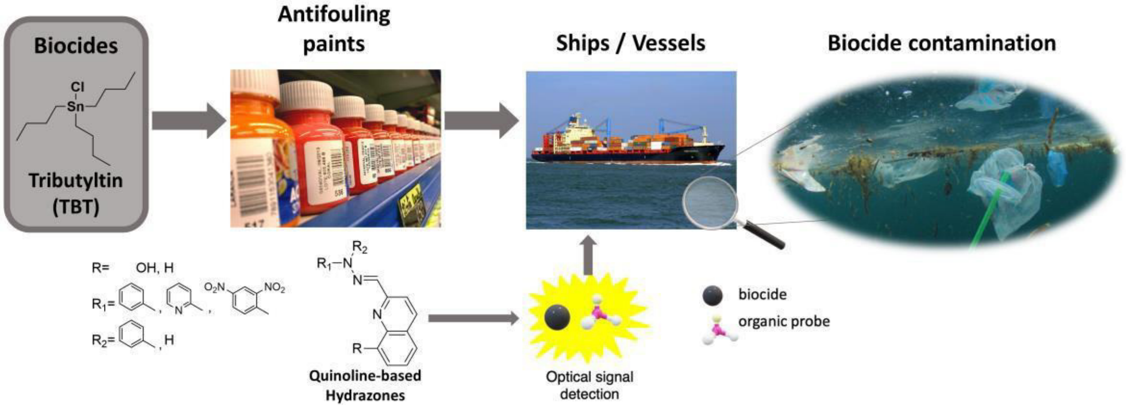


Figure 1: Biocide contamination of aquatic environments and quinoline-based hydrazones as TBT optical chemosensors.

References

[1] Laranjeiro, F.; Sánchez-Marín, P.; Oliveira, I. B.; Galante-Oliveira, S.; Barroso, C. *Environ. Pollut.* **2018**, *232*, 411–421.
[2] Sousa, R. P. C. L.; Figueira, R. B.; Costa, S. P. G.; Raposo, M. M. M. *ACS Sens.* **2020**, *5* (12), 3678–3709.

Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia (FCT) and FEDER (European Fund for Regional Development)-COMPETE-QRENEU for financial support through the Chemistry Research Centre of the University of Minho (Ref. CQ/UM UID/QUI/00686/2020), and a PhD grant to R. P. C. L. Sousa (SFRH/BD/145639/2019). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). This work was developed with support of computing facilities provided by the Project "Search-ON2: Revitalization of HPC infrastructure of UMinho" (NORTE-07-0162-FEDER-000086), co- funded by the North Portugal Regional Operational Programme (ON.2 – O Novo Norte), under the National Strategic Reference Framework (NSRF), through the European Regional Development Fund (ERDF).

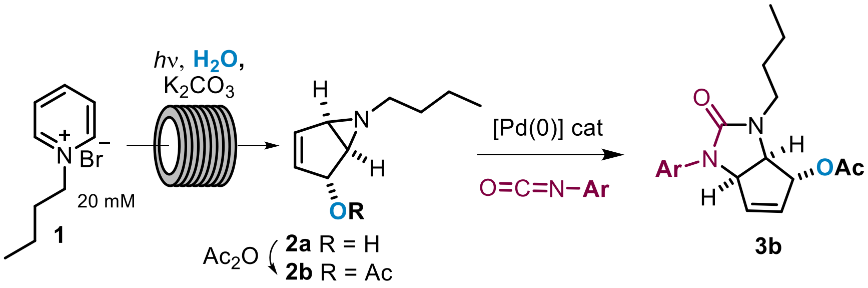
SYNTHESIS OF IMIDAZOLIDINONES THROUGH PD-CATALYZED CYCLOADDITION OF BICYCLIC AZIRIDINE WITH ISOCYANATES

Mariana Crespo Monteiro,[1]Carlos Afonso,[1] Filipa Siopa[1*]

[1]Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal.
*filipasiopa@ff.ulisboa.pt

Nitrogen-containing heterocycles can have several applications in the pharmaceutical industry since they contain a wide spectrum of biological activities. Imidazolidinones have shown activity against leukemia, lung cancer and metabolic disorders [1]. These cyclic urea frameworks can be obtained through transition-metal-catalyzed intermolecular cycloaddition using an aziridine moiety as starting material. These reactions often provide effective one-step procedures that result in heterocyclic derivatives, that are challenging to access through conventional approaches [2,3].

We have previously described the photoreaction of pyridinium salt **1** into the corresponding bicyclic aziridine **2a** under continuous-flow [4,5]. Additionally, we reported that palladium-catalyzed ring opening of bicyclic aziridine **2a-b** with active methylenes presented a new S_N2' selectivity [6]. In this study, the reaction between bicyclic aziridine **2b** and several isocyanates, in the presence of Pd(0)-catalyst is presented (**Scheme 1**). The reactions proceed through ring opening of the aziridine moiety, with the formation of the π-allylpalladium complex, followed by cyclization via nucleophilic addition of nitrogen to the isocyanate, affording regioselectively imidazolidinones **3b**.



Scheme 1: Pd-catalyzed reaction of bicyclic aziridine **2b** with isocyanates.

References
[1] F. Xu, S.A. Shuler, D.A. Watson, Angew. Chem. Int. Ed., 57 (2018) 12081.
[2] C. Dong, L. Xie, X. Mou, Y. Zhong, W. Su, Org. Biomol. Chem., 8 (2010) 4827.
[3] R. Shintani, T. Tsuji, S. Park, T. Hayashi, J. Am. Chem. Soc., 132 (2010) 7508.
[4] F. Siopa, J.P.M. António, C.A.M. Afonso, Org Process Res Dev, 22 (2018) 551.
[5] M.A.G. Fortunato, C.P. Ly, F. Siopa, C.A.M. Afonso, Methods Protoc., 2 (2019) 67.
[6] J.A.C. Oliveira, G. Kiala, F.Siopa, A. Bernard, G. Gontard, J. Oble, C.A.M. Afonso, G. Poli, Tetrahedron , 76 (2020) 1.

Acknowledgments
The authors acknowledge the Fundação para a Ciência e Tecnologia for financial support (UIDB/04138/2020, UIDP/04138/2020 and 2022.08559.PTDC). The project leading to this application has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 951996.

A FACILE METAL-CATALYZED APPROACH TOWARDS FUNCTIONALIZED AZAINDOLES

Joana R. M. Ferreira,[1,2] Bruna Guerreiro,[1] Samuel Guieu[2,3] M. Manuel B. Marques[1,*]

[1] LAQV-REQUIMTE, Department of Chemistry, School of Science and Technology, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; [2] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal; ;
[3]CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3010-193 Aveiro, Portugal.
*msbm@fct.unl.pt

Azaindoles are considered an attractive N-heterocyclic scaffold with a privileged structure in medicinal chemistry, however they rare in nature [1]. Azaindoles, besides being indole bioisosteres, present a synthetic challenge since the classical indolization methods cannot be applied to their synthesis. New azaindole synthetic approaches have been developed in our group during the last years, involving one-pot reactions catalysed by palladium such as Sonogashira or C–H activation reaction [2, 3]. In this work, we have been investigating a new approach to obtain (aza)indole derivatives exclusively substituted at the C-3 position, in a one-pot manner involving metal-catalyzed reactions (**Figure 1**).

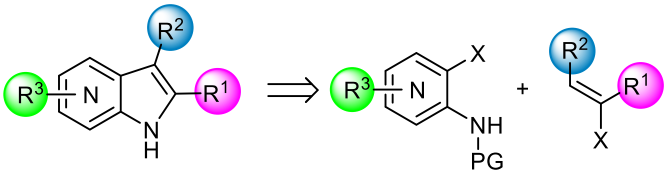


Figure 1: Proposed retrosynthetic analysis of the of (aza)indole scaffold.

References
[1] D. R. Motati, R. Amaradhi, T. Ganesh, Bioorg. Med. Chem., 28 (2020) 115830.
[2] S. I. Purificação, M. J. D. Pires, R. Rippel, A. S. Santos, M. M. B. Marques, Org. Lett., 19 (2017) 5118.
[3] A. S. Santos, M. M. Martins, A. C. Mortinho, A. M. S. Silva, M. M. B. Marques, Tetrahedron Lett., 61 (2020) 152303.

Acknowledgments
Thanks are due to University of Aveiro, FCT/MEC, Centro 2020 and Portugal2020, the COMPETE program, and the European Union (FEDER program) via the financial support to the LAQV-REQUI*M*TE (UIDB/50006/2020), to the CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020), financed by national funds through the FCT/MCTES, to the Portuguese NMR Network. SG is supported by national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. J. R. M. F. thanks FCT and ESF (European Social Fund) through POCH (Programa Operacional Capital Humano) for her PhD grant (UI/BD/151272/2021). The authors also appreciate the support of the Associate Laboratory for Green Chemistry—LAQV, which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). We thank FC&T for funding the project PTDC/QUI-QOR/0712/2020.

CULTIVATION OF *CHLORELLA VULGARIS* IN WINERY WASTEWATER FOR NUTRIENT REMOVAL AND BIOMASS PRODUCTION

Leonilde Marchão[1], Laura Rodriguez[2], Cintia Gómez-Serrano [3,4], Gabriel Acién [3,4], José A. Sánchez Pérez[3,4], Marco S. Lucas [1]

[1]Chemistry Centre - Vila Real (CQVR) and Department of Chemistry, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal, [2]Build Engineering SRL, Italy, [3]Department of Chemical Engineering, University of Almería, 04120, Almería, Spain, [4]CIESOL Solar Energy Research Centre, Joint Centre University of Almería-CIEMAT, 04120, Almería, Spain.
*leonildem@utad.pt

Wine making generates a large amount of liquid effluents, referred as winery wastewaters (WW) which are mainly originated in washing operations during grape harvesting, pressing and rinsing of fermentation tanks and other equipment. Due to the high content of biodegradable compounds, WW treatment technologies usually involve the use of biological processes [1]. Among those, microalgae, particularly *Chlorella*, have proven to be effective as wastewaters can be used as cheap nutrient sources for microalgal biomass production that could be a source for proteins, lipids and high added value products and used as a biofertilizer [2,3]. After small-scale trials to investigate the potential of *Chlorella vulgaris* for being grown in WW, the process was up-scaled using outdoor thin-layer cascade reactors operated in semi-continuous mode (dilution rate of 0.3 day^{-1}) with a working volume of 500 L and at a culture depth of 2 cm. The medium was made by simulated WW supplemented with nutrients from commercial fertilisers. It was assessed the nutrient recovery capacity of the microalga as well as the composition of the biomass produced and its plant biostimulant effects. A control run was performed with a culture medium formulated using only commercial fertilisers. When grown in WW, *C. vulgaris* achieved a maximum biomass productivity of 390 $mg \cdot L^{-1} \cdot day^{-1}$, while the nitrates, phosphates, carbon oxygen demand and total polyphenols removal capacities were 100, 74.6, 95.2 and 80.8 %, respectively. Regarding the macromolecular composition (**Table 1**), differences were observed between the lipid content of the biomass, as the lipids production was enhanced when the microalga was grown in wastewater. Both media produced a protein-rich biomass. Finally, the biomass showed auxin-like activity, after assessing the adventitious root induction of Soybean and no major differences were observed between the culture media. When applying an extract at 2.0 $g \cdot L^{-1}$ of biomass grown in fertilisers and WW, the adventitious root formation in soybean was 397% and 440%, respectively (100% formation in control samples, treated with only distilled water). Overall, the results of the present study suggest the potential of producing a protein-rich *C. vulgaris* biomass using winery wastewater that could be used to develop biostimulants.

Table 1: Macromolecular composition of C. *vulgaris*. Results are the average of three independent determinations ± standard deviation.

	Protein ($g \cdot 100\ g^{-1}$)	**Carbohydrates** ($g \cdot 100\ g^{-1}$)	**Lipids** ($g \cdot 100\ g^{-1}$)	**Ash** ($g \cdot 100\ g^{-1}$)
Control (fertilisers medium)	59.4 ± 8.8	16.0 ± 0.3	11.7 ± 8.6	16.7
Simulated WW	49.7 ± 5.4	16.6 ± 0.6	20.8 ± 4.8	12.9

References

[1] C. Amor, L. Marchão, M. S. Lucas, J. A. Peres, Water, 11, 2 (2019) 205
[2] L. Marchão, J. R. Fernandes, A. Sampaio, J. A. Peres, P. B. Tavares, M. S. Lucas, Water Res., 203 (2021) 117464
[3] A. Morillas-España, Á. Ruiz-Nieto, T. Lafarga, G. Acién, Z. Arbib, and C. V. G. López, Biology, 11 (2022) 1086

Acknowledgments

Leonilde Marchão acknowledges the financial support provided by FCT - Portuguese Foundation for Science and Technology (PD/BD/150259/2019), under the Doctoral Programme “Agricultural Production Chains – from fork to farm” (PD/00122/2012). Authors also acknowledge the OBTain project (NORTE-01-0145-FEDER-000084), co-financed by the European Regional Development Fund (ERDF) through NORTE 2020, and FCT for the financial support to CQVR (UIDB/00616/2020).

SEQUENTIAL PROCESSING OF *PINUS RADIATA* BARK WITH SCCO$_2$ AND AN IONIC LIQUID CATALYST YIELDS ABUNDANT RESIN ACIDS AND ALKANOIC ACIDS ENRICHED IN SUBERIN

Artur Bento,[1] Fernando Neiva Nunes,[1] Rita Escórcio,[1] Stefan J. Hill,[2] Manuel N. Melo,[1]
Cristina Silva Pereira[1*]

[1]Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa (ITQB NOVA), Av. da República, 2780–157, Oeiras, Portugal. [2]Scion, Private Bag 3020, Rotorua, New Zealand,
*spereira@itqb.unl.pt

The bark of *Pinus radiata* has potential as a sustainable source of high-value compounds, but its complex composition and high heterogeneity make it difficult to use in advanced biorefinery applications. Currently, most of the bark is burnt for energy and heat[1]. However, the bark contains valuable phenolic extractives and suberin, which can be used to develop innovative materials with broad bactericidal properties[2,3]. To simplify downstream processing, a green strategy involving sequential extraction of lipophilic bark constituents and suberin was developed using scCO$_2$ (40, 50 or 60 ºC / 200, 350 or 500 bar) and a biocompatible ionic liquid catalyst. The resulting scCO$_2$ extracts were rich in resin acids, while further extraction of the bark yielded suberin with an idiosyncratic high abundance of alkanoic acids[4].

After setting a green strategy for sequential extraction of lipophilic bark constituents and suberin, our current studies are targeting the upscaling of the suberin isolation process and a better understanding of suberin aggregation and self-assembly. Specifically, coarse grain simulations are being used to investigate how suberin particles interact with each other. These simulations will provide insights into the behaviour of suberin particles, and the results will aid in the development of innovative suberin-based materials, composites and blends. These findings provide opportunities for developing new value chains for the bark's major lipophilic compounds and suberin. Further development and complementary techno-economic analyses are needed to advance this promising opening bark biorefinery study.

References

[1] G. Thornburgh, Energy Technol. (Wash., D.C.); (United States) 1980, 7.
[2] E. Aspé, K. Fernández, Ind Crops Prod 2011, 34, 838–844.
[3] M. Jerez, A. Selga, J. Sineiro, J. L. Torres, M. J. Núñez, Food Chem 2007, 100, 439–444.
[4] A. Bento, R. Escórcio, A. S. Tomé, M. Robertson, E. C. Gaugler, S. J. Malthus, L. G. Raymond, S. J. Hill, C. Silva Pereira, Ind Crops Prod 2022, 185, 115172.

Acknowledgments

Funding for this work was obtained from the NZ Ministry of Business, Innovation, and Employment under Contract CO4X1802 Bark Biorefinery: Unlocking New Hydrophobic Polymers; from Portugal2020 and FEDER under the projects “PinusResina” (PDR2020-101-031905) and “BIOPINUS” (Ref. 13/SI/2020-072630); and from Fundação para a Ciência e Tecnologia (FCT) by Project MOSTMICRO ITQB with refs UIDB/04612/2020 and UIDP/04612/2020, and LS4FUTURE Associated Laboratory (LA/P/0087/2020). The NMR data were acquired at CERMAX, ITQB-NOVA, Oeiras, Portugal with equipment funded by FCT.

OPTIMIZATION OF ULTRASOUND- AND HEAT-ASSISTED EXTRACTIONS OF PHENOLIC COMPOUNDS FROM OLIVE WASTES FOR FOOD APPLICATIONS

Joana Madureira[1,2,3,4], Bruno Melgar[2], Bianca Albuquerque[2,3], Maria Inês Dias[2,3], José Pinela[2,3], Ricardo C. Calhelha[2,3], Fernanda M.A. Margaça[1,5], Celestino Santos-Buelga[4,6], Lillian Barros[2,3], Sandra Cabo Verde[1,5]*

[1]Centro de Ciências e Tecnologias Nucleares (C^{2}TN), Instituto Superior Técnico, Universidade de Lisboa, Portugal; [2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Portugal; [3]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Portugal; [4]Grupo de Investigación en Polifenoles (GIP-USAL), Facultad de Farmacia, Universidad de Salamanca, Spain; [5]Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Portugal; [6]Unidad de Excelencia Producción, Agrícola y Medioambiente (AGRIENVIRONMENT), Parque Científico, Universidad de Salamanca, Spain.
*sandracv@ctn.tecnico.ulisboa.pt

Olive pomace is considered a harmful waste from the olive oil industry although containing considerable amounts of phenolic compounds with potential use as food bioactives [1]. The aim of this work was to study the feasibility of ionizing radiation, a clean and eco-friendly technology, to possibly improve the extractability of those compounds as well as to evaluate the most suitable extraction methodology to enhance their bioactive properties.

The irradiation experiments were carried out at room temperature in a Co-60 semi-industrial facility (Campus Tecnológico e Nuclear). Hydroxytyrosol was found as the most abundant compound in the extracts of olive pomace, followed by hydroxytyrosol-1-β-glucoside, tyrosol, luteolin-7-*O*-rutinoside, oleuropein aglycone isomer 1, and verbascoside. Furthermore, gamma radiation at 5 kGy improved the extractability of these compounds by 2-fold, and the antioxidant activity of the samples [2]. Heat- (HAE) and ultrasound-assisted extraction (UAE) were performed to optimize the extraction of the major compounds present in the extracts from irradiated olive pomace. Comparing the obtained optimal conditions, UAE reduced the extraction time and the solvent consumption (t = 28 min, P = 490 W and S = 7.3% ethanol for UAE; t = 120 min, T = 85 ºC and S = 76% ethanol for HAE) when compared to HAE, and also led to higher extraction yields (UAE yield = 30%; HAE yield = 13.7%). Nevertheless, HAE extract presented higher antioxidant, antidiabetic, anti-inflammatory and antibacterial activities. Moreover, HAE extract also showed higher cytotoxic effect for breast adenocarcinoma (MCF-7) cell line [3].

The overall results demonstrated that 5 kGy absorbed dose can improve the extractability of bioactive compounds from the olive waste and that the extracts obtained by the optimal conditions of HAE presented enhanced bioactivities. These extracts could be incorporated as natural ingredients in minimally processed fruits and other foods to extend their shelf life, supporting the interest of food industries in developing new ingredients with bioactive potential from agro-industrial wastes to replace the synthetic ones, and contributing for the sustainability of both agro-industrial sector and environment.

References

[1] M.A. Nunes et al., Science of the Total Environment, 644 (2018) 229-236.
[2] J. Madureira et al., Science of the Total Environment, 727 (2020) 138706.
[3] J. Madureira et al., Food & Function, (2023).

Acknowledgments

The authors are grateful to Foundation for Science and Technology (FCT, Portugal): UIDB/04349/2020, UIDB/00690/2020, UIDP/00690/2020, SFRH/BD/136506/2018; European Regional Development Fund (ERDF): "BIOMA" (POCI-01-0247-FEDER-046112) and "OliveBIOextract" (NORTE-01-0247-FEDER-049865) and "NORTE2020" (NORTE-06-3559-FSE-00018, BM contract); Junta de Castilla y León (Spain): SA093P20 and CLU-2018-04; "UCASUL - União de Cooperativas Agrícolas do Sul" agro industrial cooperative; Technological Unit of Radiosterilization (University of Lisbon) for the samples irradiation.

011

EVALUATION OF THE PHENOLIC PROFILE AND BIOACTIVE POTENTIAL OF PORTUGUESE AND ALGERIAN PUMPKIN BY-PRODUCTS

Maria G. Leichtweis,[1,2] Adriana K. Molina,[1,2] Tânia C. S. Pires,[1,2] Maria Inês Dias,[1,2] Ricardo Calhelha[1,2,] Khaldoun Bachari,[3] Borhane E. C. Ziani,[3] M. Beatriz P. P. Oliveira,[4] Carla Pereira,[1,2,*] Lillian Barros[1,2]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253Bragança, Portugal; [2]Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal; [3]Centre de Recherche Scientifique et Technique en Analyses Physico- Chimiques-CRAPC, Bou Ismaïl 42004, Algeria; [4]REQUIMTE—Science Chemical Department, Faculty of Pharmacy, Universityof Porto, Rua Jorge Viterbo Ferreira no. 228, 4050-313 Porto, Portugal.
*carlap@ipb.pt

Pumpkin, a globally appreciated fruit, possesses a balanced nutritional profile and valuable biological and pharmacological properties. However, currently, the industrial processing of this fruit still focuses on the pulp, while large volumes of by-products are wasted. Considering the potential content of high value-added compounds in this fruit parts, like seeds and peel [1], the present study proposed the seeds, peel, and fibrous strands from three different genotypes that are economically significant in Portugal and Algeria to produce bioactive extracts. In order to support their usage as preservatives, their phenolic content and bioactivity were assessed. The hydroethanolic extracts (80:20 ethanol/water) were obtained by maceration, and their phenolic profile was analyzed by HPLC-DAD-ESI/MS, with a tentative identification followed by quantification. Also, the antioxidant properties were assessed through two cell-based assays (OxHLIA and TBARS) and the antimicrobial capacity was tested against eight bacterial and two fungal strains. In terms of phenolic profile, eight compounds were found, six of which belonging to the flavonoid family. The Portuguese 'Common Pumpkin' peel showed the most diversified profile and also the highest concentration of total phenolic compounds (9.4 ± 0.3 mg/g), with considerable concentrations of (-)-epicatechin (4.58 ±0.08 mg/g). Despite the different phenolic composition, all samples presented relevant bioactive properties.

Regarding the antioxidant capacity, the seeds of 'Butternut Squash' from both countries stood out, while the fibrous strands of Portuguese 'Butternut Squash' and the seeds of Algerian 'Gold Nugget Pumpkin' revealed the strongest antimicrobial activity. In addition, the potential safety of the extracts was verified, where none of the samples showed toxicity against a primary culture of non-tumor porcine liver cells (PLP2) up to 400 g/mL. The identification of bioactive compounds in pumpkin byproducts highlights their significant potential as a source of bio-based preservatives, which can promote consumers' health and contribute to a circular economy.

References

[1] M. G. Leichtweis, M. B. P. Oliveira, I.C.F.R. Ferreira, C. Pereira, L. Barros, Antioxidants, 10 (2021), 827.

Acknowledges

The authors are grateful to the Foundation for Science and Technology, P.I., (FCT, Portugal) through national funds FCT/MCTES to CIMO (UIDB/00690/2020 and UIDP/00690/2020), SusTEC (LA/P/0007/2021) and UIDB/50006/2020; national funding by FCT, P.I., through the institutional scientific employment program-contract for M.I.D., R.C., C.P. and L.B. contracts and M.G. and A.K.M. PhD grants (2020.06706.BD and 2020.06231.BD, respectively). To FCT, P.I., within the scope of the Project PRIMA Section 2—Multi-topic 2019: PulpIng (PRIMA/0007/2019).

OPTIMIZATION OF A GDME-HPLC-DAD-MS/MS METHODOLOGY FOR THE SCREENING OF VOLATILE CARBONYL COMPOUNDS IN WOOD-BASED PANELS

Fátima Daniela Gonçalves,[1*] Luísa Hora Carvalho,[2,3] José António Rodrigues,[1] Rui Miguel Ramos[1]

[1]LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, Porto, 4169-007, Portugal; [2]DEMad–Departamento de Engenharia de Madeiras, Instituto Politécnico de Viseu, Av. Cidade Politécnica, Viseu, 3504-510, Portugal; [3]LEPABE–Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal.
*up201805253@up.pt

Over the years, the amount of time spent indoors has increased due to modern lifestyle, bringing special attention to indoor air quality and the potential impact of poor indoor air quality on human health [1,2]. A possible source of indoor air pollution is furniture and building materials made from wood-based panels (WBPs), as they emit volatile organic compounds (VOCs).

WBPs refer to wood products made from fibres, particles, or veneers such as particleboards (PBs), medium-density fibreboards (MDFs), oriented strand boards, plywood, and others. To produce a panel, an adhesive is added to the fibres or particles, creating a mixture that is laid in a press and heated until the adhesive hardens, forming a solid panel [3]. The emission of VOCs can be a consequence of the raw materials, chemical additives, or processes used during panel production.

This study employed gas-diffusion microextraction (GDME) [4,5] to extract volatile carbonyls from PBs and MDFs, coupled with a derivatization reaction with 2,4-dinitrophenylhydrazine (DNPH), followed by HPLC-DAD analysis. GDME is an innovative sample preparation technique, in which the analytes from the sample pass through a gas-permeable membrane into an acceptor solution, typically a derivatizing agent.

Various studies were conducted to validate the use of GDME, including the cleaning procedure, optimization of the GDME extraction parameters using a one variable at a time (OVAT) approach and two different experimental designs (2^4 factorial design for screening and a Box-Behnken design), evaluation of the precision of the extraction, variability of PB and MDF samples, besides other quantitative preliminary studies.

To separate the derivatized carbonyl compounds in HPLC-DAD, gradient elution methods and different chromatographic columns were tested. HPLC-DAD-MS/MS studies were performed to identify the volatile carbonyl compounds extracted from PBs and MDFs.

References

[1] M. Jantunen, J. J. K. Jaakkola, M. Krzyzanowski, WHO Reg. Publ. Eur. Ser. 78 (1997).
[2] T. Adamová, J. Hradecký, M. Pánek, Polymers. 12 (2020) 2289.
[3] Wood-Based Panels: An Introduction for Specialists, M. Irle, M. Barbu, P. Niemz, L. Carvalho, J. Martins, C. Costa, L. Muszyski, M. Launey, M. Sernek, M. Dunky, J. Aderhold, B. Plinke, O. Treusch, M. Ohlmeyer, W. Paul, London, Brunel University Press, 2010.
[4] J. G. Pacheco, I. M. Valente, L. M. Gonçalves, J. A. Rodrigues, A. A. Barros, J. Sep. Sci. 33 (2010) 3207-3212.
[5] P.F. Brandão, R.M. Ramos, P.J. Almeida, J.A. Rodrigues, J. Agric. Food Chem. 65 (2017) 1037-1042.

Funding

This work received financial support from national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through project PTDC/CTM-PAM/1348/2021.

Acknowledgements

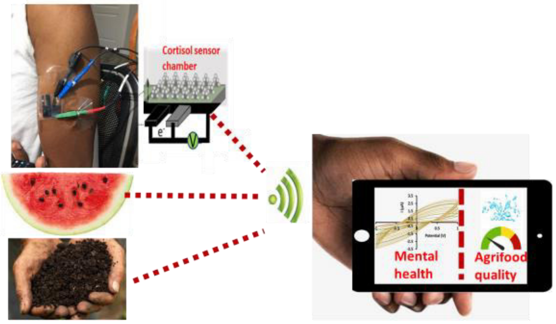
This work was supported through the project UIDB/50006/2020 and UIDP/50006/2020, funded by FCT/MCTES through national funds and CEECIND/04259/2017 (through the Individual Call to Scientific Employment Stimulus).

PAPER BASED POINT OF NEED (PON) COLORIMETRIC AND MULTIPLEXED ELECTROCHEMICAL SMARTPHONE BASED SENSORS FOR CITIZEN CHEMICAL SENSING ANALYTICS

Samuel M. Mugo[1*], Scott V. Robertson[1,] Weihao Lu[,1]
Physical Science Department, MacEwan University, 10700 104 Ave, Edmonton, Alberta,Canada
*mugos@macewan.ca

Chemical sensors are a major segment of Internet of Things (IoT) devices are key drivers to the emerging fourth industry revolution (industry 4.0)—that broadly speaking aims to create 'self-aware' seamlessly interconnected sustainable production ecosystems.

Our research group is focused on developing printed paper-based point of need (PON) colorimetric and electrochemical sensors for real-time wireless monitoring of water and soil nutrients for precision agriculture, as well as stress metabolites sweat analytics for mental health assessment in humans.



Schematic depiction of electro-colorimetric smartphone sensors

Fabricated by layer by layer (LbL) integration of analyte selective biomimetic molecular receptors and transduction on a smartphone, in this presentation we will demonstrate our multi-architecture sensors for in-situ multiplex colorimetric and electrochemical detection of soil quality indicators namely, redox potential, pH, cation exchange, phosphates and nitrites [1-2]; as well as lactic acid [3], adrenaline [4]cortisol [5-7] and adrenaline, detection in human sweat [1-3].

Our embedded multiplex sensors are aimed to be enabling proactive diagnostics technology for realization of environmental, social, and economic aspects that align with the United Nation's Sustainable Development Goals (UN SGDs), particularly sustainable smart agriculture, climate change, food security, environmental conservation, and in general, equity in global societies wellbeing.

References

[1] S.M. Mugo, W. Lu, S. Lemieux, Microchimica Acta, 189 (2022), 1.
[2] Mugo, S.M., Lu, W. Dhanjai, S. Robertson Biosensors (Basel), 12 (2022), 1001.
[3] S. M. Mugo, Dhanjai, J. Alberkant**.** IEEE sensor, 20 (2020), 5741**.**
[4] Dhanjai, N. Yu S.M. Mugo. Talanta, 2019, 204, 602-606.
[5] S.M. Mugo, W. Lu, M. Wood, S. Lemieux, Electrochemical Science Advances, 2(2022).e2100039.
[6] J. Alberkant, S. M. Mugo. Analytical Bioanalytical Chemistry, 316 (2020), 1825.
[7] S.M. Mugo, W. Lu, S. Robertson, *Biosensors* (Basel), *12*(2022), 854.

Acknowledgments

The Mugo research group acknowledges funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and MacEwan University Research.

EXPLAINABLE ARTIFICIAL INTELLIGENCE METHODS IN MACHINE LEARNING MODELS TO PREDICT STANDARD VAPORIZATION ENTHALPIES

José Ferraz-Caetano,[1*] Filipe Teixeira,[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]CQUM – Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
*jose.caetano@fc.up.pt

The determination of thermodynamic properties is a key asset in developing chemical processes, but most accurate experimental measurements are unfeasible due to their impractical time-consuming and costly techniques. As current theoretical methods require high computational costs and complex specialised programming skill sets, swift alternatives are needed to manage the prediction accuracy/speed trade-off. To this end, alternative Artificial Intelligence (AI) based models were developed to predict accurate chemical molecular properties[1]. In particular, Machine Learning (ML) algorithms have the advantage of yielding fast-sustained statistical predictions instead of mechanical-based calculations, reducing the need for chemical intuition input. As ML models are more user-friendly, posing as a credible alternative to traditional computational predictions, they still present two major drawbacks. They often cannot predict values under the 1 kcal mol^{-1} validation threshold[2], readily matching experimental precision beyond restricted molecular families. Also, ML models frequently lack chemical explainability on their predictions, being incapable of interpreting the physical meaning of their statistical based results.

In this communication, we report how we bypassed existing obstacles in ML property determinations, using a Data Science method to build a fast, accurate and explainable model for complex chemical thermodynamic predictions. We developed a model to predict the standard vaporization enthalpy ($\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\circ}$) of organic molecules through an explainable ML approach **(Figure 1)**. A diverse dataset of 1392 different molecules was built, a wide comprehensive library of documented experimental values of $\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\circ}$ and molecular open-source physicochemical descriptors. Despite dataset diversity, our supervised regression algorithm successfully outperformed current $\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\circ}$ predictions with an average error of 0.57 kcal mol^{-1} and 97% accuracy. Our models were further validated through an established external database of known compounds, yielding a maximum error of 2.2%. We also present an explainable ML framework to interpret chemical model predictions, revealing how topological, descriptive and electronic features influence algorithm performance, arguing this method to be expanded towards other chemical property predictions.

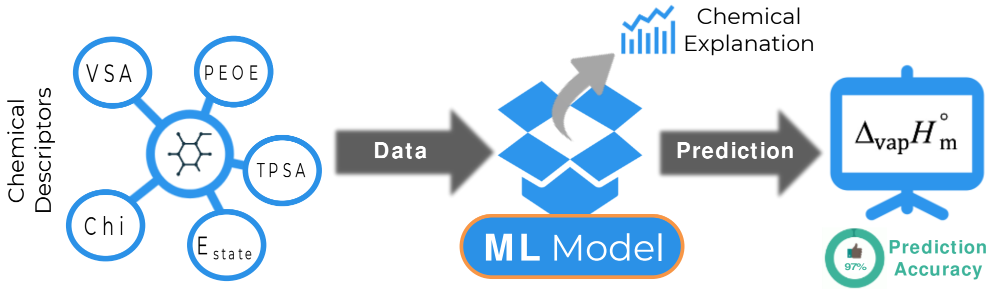


Figure 1: Graphical depiction of the reported ML model development workflow.

References

[1] K.T. Butler, D.W. Davies, H. Cartwright, O. Isayev, A. Walsh, *Nature* 559 (2018), 547-555.
[2] B. Ruscic, *International Journal of Quantum Chemistry* 114:17 (2014), 1097-1101.

Acknowledgments

This work received financial support from Fundação para a Ciência e Tecnologia (FCT/MCTES) through the projects UIDB/50006/2020, and PTDC/QUIQIN/30649/2017 awarded to LAQV-REQUIMTE. José Ferraz-Caetano thanks FCT and MIT Portugal for the PhD Fellowship SFRH/BD/151159/2021

DEGRADATION OF FLUORINATED COMPOUNDS IN THE TROPOSPHERE: AN ACCURATE COMPUTATIONAL PROTOCOL

Luís P. Viegas[1]

[1]Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS), Department of Chemistry, University of Coimbra,
Coimbra 3004-535, Portugal.
*lpviegas@ci.uc.pt

The impact of hydrofluorocarbons (HFCs) on global warming can be hundreds to thousands of times greater than that of CO_2. With the rapid rise of HFC emissions and their projected catastrophic effects on the atmosphere and climate, the Kigali Amendment of 2016 [1] seeks to drastically reduce the global production and consumption of HFCs, thus contributing to the Paris agreement target of limiting the global temperature rise below 2 degrees Celsius. For this reason, new ideas and green technologies are necessary to achieve the Kigali goals and mitigate climate change effectively. Based on recent results [2-4], we demonstrate that our cost-effective computational protocol [5,6] based on multiconformer transition state theory (MC-TST) and a method for performing transition state sampling called constrained transition state randomization (CTSR) [2] is capable of predicting with unprecedented accuracy the rate coefficients of the OH-initiated degradation reactions of several families of saturated organic compounds that could replace HFCs. Specifically, our calculations based on the M08-HX/pcseg-2 level of theory yield rate coefficients that agree with the recommended experimental values [7], on average, to within a factor of two.

Furthermore, the fitted Arrhenius–Kooij curves based on the improved semiclassical TST tunneling correction [8] show a good agreement with the recommended experimental Arrhenius fits, implying that MC-TST/CTSR temperature-dependent data can be used to model reactions in the atmosphere in situations where experimental information is not available. Consequently, our computational approach has the potential not only to deliver the required fundamental knowledge but also to actively take part in a critical scientific endeavor.

References

[1] E. A. Heath, Int. Leg. Mater., 56 (2017) 193.
[2] L. P. Viegas, Chem. Phys. Lett., 803 (2022) 139829.
[3] L. P. Viegas, J. Phys. Org. Chem., 36 (2023) e4470.
[4] L. P. Viegas and F. Jensen, Environ. Sci.: Atmos., DOI: 10.1039/d2ea00164k (2023).
[5] L. P. Viegas, J. Phys. Chem. A, 122 (2018) 9721.
[6] L. P. Viegas, J. Phys. Chem. A, 125 (2021) 4499.
[7] M. R. McGillen, W. P. L. Carter, A. Mellouki, J. J. Orlando, B. Picquet-Varrault and T. J. Wallington, Earth Syst. Sci. Data, 12 (2020) 1203.
[8] A. F. Wagner, J. Phys. Chem. A, 116 (2014) 13089.

Acknowledgments

The Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS) is supported by the Portuguese Foundation for Science and Technology (FCT) through projects UIDB/QUI/0313/2020, UIDP/QUI/0313/2020 and LA/P/0056/2020 (national funds). L. P. V. acknowledges FCT for an Assistant Researcher grant.

ELECTROCHROMIC WINDOWS BASED ON LUMINESCENT ACRYLATE/IONOSILICAS

Daniela Pinheiro,[1*] Rui F. P. Pereira,[2] Elvira Fortunato,[3] Rute A. S. Ferreira,[4] Verónica de Zea Bermudez,[1] Maria Cristina Gonçalves[1]

[1]Chemistry Department and CQ-VR, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal; [2]Chemistry Department and Chemistry Centre, University of Minho, 4710-057 Braga, Portugal; [3]CENIMAT/I3N, Departamento de Ciência dos Materiais, Universidade Nova de Lisboa and CEMOP-UNINOVA, 2829-516 Caparica, Portugal; [4]Physics Department and CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal.
*danielap@utad.pt

Climate change and environmental problems are existential threats to the world. Therefore, it is necessary, not only to substitute fossil fuels for renewable energies, but also to reduce our energy consumption. The buildings sector represents 30-40% of the primary energy worldwide [1], with traditional windows wasting ~30% of the energy for heating, cooling and lighting the buildings. Electrochromic devices (ECDs) that can reversibly change color through the application of a low electric voltage (1.0-3.0 V) [2] have emerged as a promising technology and have high potential when applied to windows. Poly(methyl methacrylate) (PMMA)-based composite films doped with lanthanide-doped sol–gel derived ionosilicas were previously proposed for ECDs [3]. Nevertheless, some challenges remained to be addressed, the most critical being the poor solubility of PMMA in the ionic liquid present in the formulation of these materials. To avoid this drawback, in this work novel lanthanide-containing acrylate/ionosilicas (AC/IS-Ln, Ln = Tb^{3+}, Eu^{3+}) were prepared by the sol-gel method. The resulting transparent, homogeneous and luminescent hybrid materials were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, atomic force microscopy, contact angle measurements, ionic conductivity and photoluminescence spectroscopy, and successfully employed as electrolytes in luminescent ECD prototypes (**Figure 1**). The ECD device doped with AC/IS-Eu showed good cycling stability with reproducible bleaching/coloring over 50 chronoamperometry cycles and high coloration efficiency (CE) values CEin/CEout in the visible (-89/+98 $cm^2.C^{-1}$) and near-infrared (-126/138 $cm^2.C^{-1}$) spectral regions.

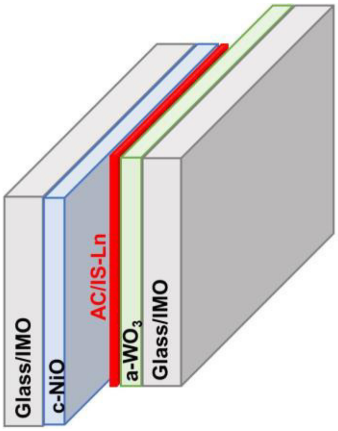


Figure 1: Schematic representation of glass/IMO/a-WO_3/AC/IS-Ln/c-NiO/IMO/glass ECD configuration (where IMO, a-WO_3, c-NiO stand for indium molybdenum oxide, amorphous tungsten oxide and crystalline nickel oxide, respectively).

References

[1] M.W. Akram, M.F. Mohd Zublie, M. Hasanuzzaman, N.A. Rahim, Sustainability 14(3) (2022) 1316.
[2] M. Casini, Energy 119 (2018) 923-934.
[3] M.A. Cardoso, S.F.H. Correia, H.M.R. Gonçalves, R.F.P. Pereira, S. Pereira, T.M.R. Maria, M.M. Silva, A.J.M. Valente, E. Fortunato, R.A.S. Ferreira, V. de Zea Bermudez, J. Sol-Gel Sci. Technol. 101(1) (2022) 58-70.

Acknowledgments

This work was funded by project I&D&I OBTain, operation nº NORTE-01-0145-FEDER-000084), co-financed by the European Regional Development Fund (FEDER) thought NORTE 2020 (Northern Regional Operational Programme 2014/2020), SOLPOWINS-Solar-Powered Smart Windows for Sustainable Buildings" (PTDC/CTM/4304/2020), CQ-VR that is supported by FCT through the projects UIDB/00616/2020 and UIDP/00616/2020 and 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)". D.P. acknowledges OBTain for post-doc grant BIPD/UTAD/19/2021. R.P. acknowledges FCTUMinho for the contract in the scope of Decreto-Lei 57/2016 57/2017.

REDUCED CHITOSAN AS AN ADSORBENT FOR METAL ION REMOVAL FROM WATER

Pedro M. C. Matias,[1*] Joana F. M. Sousa,[1] Eva Bernardino,[1] Paulo Abreu,[1] Jorge Marques,[1]Dina Murtinho,[1] Artur J. M. Valente[1]
[1]University of Coimbra, CQC-IMS, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal
*petermatias1998@gmail.com

The presence of heavy metals as priority pollutants in water affects negatively the environment and the living beings. Among several reported starting materials, chitosan is a biocompatible D-glucosamine polymer obtained from chitin deacetylation, with huge potential for the development of efficient adsorbents for ion metal removal. This communication describes the one-pot synthesis of reduced chitosan derivatives (RCDs) by modification of chitosan with salicylaldehyde (A), followed by reduction of the imine bonds (B) (**Figure 1**). The polymers were characterized by 1H-NMR, FTIR-ATR, TGA and SEM. In Cu(II) adsorption, RCD3, with 43% degree of modification (*DM*) and 98% degree of reduction (*DR*) (**Table 1**), was more efficient than neat chitosan, especially at low concentrations and at the best adsorption conditions (RS/L = 2.5 mg mL−1, pH = 4). By analyzing the sorption isotherms, Langmuir and Langmuir-Freundlich models were the ones that best fit the experimental data for chitosan and RCD3, respectively, suggesting a Cu(II) monolayer formation in chitosan chain [1] and a chelation reaction in RCD3 [2]. The pseudo-second order kinetic model best fitted the kinetic data, confirming the occurrence of chemisorption, explained by the formation of metal-ligand coordination bonds [3,4]. Both RCD3 and chitosan also showed higher selectivity for Cu(II) adsorption than Ni(II), Cd(II) and Pb(II). The interaction mechanism was assessed by molecular dynamic studies, which showed that the presence of the phenolic substituent groups in RCD3 allows a faster and more stable formation of a Cu(II)-polymer complex, since the metal ion spreads over the whole ring, whereas in chitosan, Cu(II) tends to be found only in some oxygen atoms.

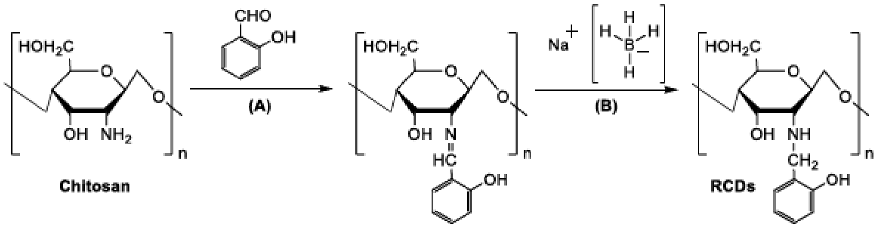


Figure 1: Synthetic approach for the reduced chitosan derivatives (RCDs) preparation.

Table 1: Solvents used in the synthesis of RCDs and respective degrees of modification (*DM*) and reduction (*DR*).

Chitosan Derivative	Step (A)	Step (B)	*DM* / %	*DR* / %
RCD1	CH_3COOH (2%)	CH_3COOH (2%):MeOH (1:1, v/v)	42	69
RCD2	CH_3COOH (2%):MeOH (1:1, v/v)	CH_3COOH (2%)	43	63
RCD3	CH_3COOH (2%):MeOH (1:1, v/v)	MeOH	43	98
RCD4	MeOH	MeOH	69	98

References

[1] K. Foo, B. Hameed, *Chemical Engineering Journal*, 156 (2010) 2–10.
[2] G. Kyzas, M. Kostoglou, N. Lazaridis, *Chemical Engineering Journal*, 152 (2009) 440–448.
[3] J. Vareda, A. Valente, L. Durães, *Adv Colloid Interface Sci*., 237 (2016) 28 – 42.
[4] M. Mende, D. Scwarz, C. Steinbach, R. Boldt, S. Schwarz, *Colloids Surf A Physicochem Eng Asp*, 510 (2016) 275–282.

Acknowledgments

This work is funded by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project BLUEBIO/0003/2019 and by the Coimbra Chemistry Center (CQC) through the project UID/QUI/00313/2020. We acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt). P.M.C. Matias thanks FCT, Portugal for the Ph. D Grant 2022.12425.BD.

SILK FIBROIN-BASED THERMOTROPIC DEVICE

Tiago A. G. Duarte[1*], João P.S. Silva[2], Rui F.P. Pereira[2], Verónica de Zea Bermudez[1]

[1]*Chemistry Department and CQ-VR, University of Trás-os-Montes e Alto Douro, Apartado 1013, 5001-801 Vila Real, Portugal*;
[2]Chemistry Center and Chemistry Department, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
*tduarte@utad.pt

Bioinspired approaches are particularly attractive for the domain of energy materials. The urgent need to transition to a greener energy scenario demands cleaner, safer, cheaper, and more efficient energy materials and devices. In the last few years these concerns and sustainability issues have prompted the scientific community to take advantage of the panoply of outstanding features offered by natural materials, such as abundance, easy, fast and clean synthesis, and eco-friendly and biodegradable properties.

While many illustrative examples of the use of polysaccharides for the development of polymer electrolytes (PEs) for electrochemical devices have been reported, [1] the same does not apply to proteins [2]. Motivated by the superior mechanical properties, self-assembly, machinability, biocompatibility, and controllable biodegradability characteristics of *Bombyx mori*-derived silk fibroin (SF), our group proposed the first PEs composed of SF, glycerol, and a lithium salts to produce electrochromic devices (ECDs) for smart windows of energy efficient buildings [3]. Green, transparent and flexible electrolyte films composed of SF, glycerol, dimethyl sulfoxide and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (IL), were later studied [4]. Maximum conductivities of 1.07 and 4.61×10^{-3} S cm^{-1}, at 22 and 100 °C, respectively, were achieved.

In the present work, aiming the development of sun-actuated thermotropic windows (TTWs) and relying on a strategy introduced recently [5], we have used SF as the key material of a thermotropic device (TTD) incorporating as active material SF-based films doped with variable concentrations of an ionanofluid (INF). The latter is composed of SF-derived carbon dots and a mixture of two ILs, one of these being 1-butyl-3-methylimidazolium chloride which displays a reversible TT effect around 30 °C associated with a *trans*–*trans* to *trans*–*gauche* conformational change of the butyl chain. A maximum conductivity of 2.27×10^{-4} S cm^{-1} was measured for the sample incorporating 200% wt. of INF at 60 ºC. Preliminary tests with a prototype TTD led to transmittance variations (ΔT) of 6/15% and 13/20% at 550/1600 nm at 45 and 60 ºC, respectively. This performance could be amplified via the surface plasmon resonance effect.

References

[1] S. C. Nunes, R. F. P. Pereira, N. Sousa, M. M. Silva, P. Almeida, F. M. L. Figueiredo, V. de Zea Bermudez, Adv. Sustainable Syst., 1, (2017) 1700070; F. M. Santos, P. C. Barbosa, R. F. P. Pereira, M. M. Silva, H. M. R. Gonçalves, S. C. Nunes, F. L. Figueiredo, A. J. M. Valente,V. de Zea Bermudez, Eur. Polym. J., 124 (2020) 109453.

[2] R. Leones, M. Fernandes, R. A. S. Ferreira, I. Cesarino, J. F. Lima, L. D. Carlos, V. de Zea Bermudez, C. J. Magon, J. P. Donoso, M. M. Silva, Pawlicka, J. Nanosci. Nanotechnol., 14 (2014) 6685; C. O. Avellaneda, D. F. Vieira, A. Al-Kahlout, S. Heusing, E. R. Leite, A. Pawlicka, and M. A. Aegerter, Sol. Energ. Mat. Sol. Cells, 92 (2008) 228.

[3] R. F. P. Pereira, F. Sentanin, A. Pawlicka, M. C. Gonçalves, M. M. Silva, V. de Zea Bermudez, Chem. Electro. Chem., 3 (2016) 1084.

[4] T. C. D. Fernandes, H. M. R. Rodrigues, F. A. A. Paz, Joana F. M. Sousa, A. J. M. Valente, M. M. Silva, V. de Zea Bermudez, R. F. P. Pereira, J. Electrochem. Soc., 167 (2020) 070551

[5] H. M. R. Gonçalves, R. F. P. Pereira, E. Lepleux, T. Carlier, L. Pacheco, S. Pereira, A. J. M. Valente, E. Fortunato, A. J. Duarte, V. de Zea Bermudez, Adv. Sustainable Syst. 3, 7 (2019) 1900047.

Acknowledgments

This work was funded by SOLPOWINS/PTDC/CTM-REF/4304/2020 and OBTAIN/NORTE-01-0145-FEDER-000084. T.A.G.D. thanks OBTAIN for his postdoc grant (BIPD/UTAD/18/2021).

THE EFFECT OF OLEATE IN THE BIOLOGICAL NITROGEN REMOVAL

SA Silva,[1,2,3*] MS Duarte,[1,2] AL Amaral,[1,2,4,5] EC Ferreira,[1,2] MS Lucas,[3] MM Alves,[1,2] DP Mesquita[1,2]

[1] CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; [2]LABBELS – Associate Laboratory, Braga/Guimarães, Portugal; [3]Chemistry Centre, Vila Real (CQVR) and Department of Chemistry, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal; [4]Polytechnic Institute of Coimbra, Coimbra Institute of Engineering, Rua Pedro Nunes, Quinta da Nora, 3030-199 Coimbra, Portugal; [5]Polytechnic Institute of Coimbra, Applied Research Institute, Rua da Misericórdia, Lagar dos Cortiços – S. Martinho do Bispo, 3045-093 Coimbra, Portugal
*sergiosilva@utad.pt

Lipids can make up to 40% of the chemical oxygen demand (COD) in wastewaters and can easily be converted into long-chain fatty acids (LCFA), which can induce negative effects on biological wastewater treatment, such as inhibition and sludge flotation. The concentration of LCFAs in domestic wastewaters is typically low (around 100 mg L^{-1}) and oleate (oleic acid; C18:1) is the most commonly found unsaturated LCFA in wastewater treatment plants. Aerobic granular sludge (AGS) technology is considered a more efficient option when compared to conventional activated sludge systems due to its higher sludge concentration and retention. However, granules instability is still considered a bottleneck for these systems. The aim of this study was to evaluate the impact of oleate concentration on nitrogen removal efficiencies in AGS systems, using concentrations typical of domestic wastewaters (ranging from 1 – 114 mg L^{-1}). Ammonium removal remained stable during most of the reactor operation. However, nitrifying microorganisms were affected at the highest oleate concentration of 114 ± 4 mg L^{-1}, resulting in an approximately 20% decrease in ammonium removal and an increase in the residual nitrite concentration in the effluent. The average size of the granules increased considerably at higher oleate concentrations due to selective sludge washout of smaller granules. Previous research has shown that small granules (about 300 µm) had a higher ammonium oxidation rate than larger granules **[1]**. Total inorganic nitrogen (TIN) in the effluent was considered as the sum of ammonium, nitrite, and nitrate. Initially, nitrate was produced by ammonium nitrification, while nitrite concentration remained below 1 mg L^{-1}. The nitrate concentration increased before the addition of oleate, indicating a decrease in the denitrification capacity of the AGS, most likely due to oxygen diffusion inside the granules. However, when oleate was added to the feed, the nitrate concentration in the effluent gradually decreased, leading to an increase in TIN removal efficiency up to 94%. A clear negative correlation ($R^2 = 0.977$) was observed between the nitrate concentration in the effluent and the oleate concentration in the feed. Nitrogen removal is favoured by the decrease in oxygen concentration. Thus, oleate accumulation onto the AGS and the increase in the average size of the granules could limit oxygen diffusion to the inner layers where denitrifying organisms are present, promoting nitrate degradation. Overall, nitrogen removal in wastewaters containing oleate by AGS in an SBR was feasible. Although the ammonium removal efficiency decreased by 20%, the accumulation of oleate onto the granules increased TIN removal by limiting oxygen diffusion and enhancing the denitrification capacity of AGS.

References

[1] BN. Quoc, S. Wei, M. Armenta, R. Bucher, P. Sukapanpotharam, DA. Stahl, HD. Stensel, MKH. Winkler, Water Res. 188, (2021) 116445.

Acknowledgments

The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) under the scope of the strategic funding of UIDB/04469/2020 and UIDB/00616/2020 unit, and by LABBELS – Associate Laboratory in Biotechnology, Bioengineering and Microelectromechanical Systems, LA/P/0029/2020 and the financial support provided by OBTain project (NORTE-01-0145-FEDER-000084), European Regional Development Fund (ERDF) through NORTE 2020. The authors also acknowledge the financial support to Sérgio A. Silva through the grant SFRH/BD/122623/2016 and COVID/BD/151748/2021 provided by FCT. Daniela P. Mesquita acknowledges FCT funding under DL57/2016 Transitory Norm Programme

PETSCENT PROJECT:
OBTAINING OPTICAL SENSORS FROM PET BOTTLES

Ana M. G. Silva,[1*] Carla Queirós,[1] Paula Figueiredo,[2] Ken Lukau,[2,] Maria Inês Soares,[2]
Sofia Moreira,[2] Pedro Mendes[3]

[1] LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal; [2]Escola Secundária da Maia, Av. Luís de Camões, 4470-194 Maia, Portugal; [3]Colégio Internato dos Carvalhos, R. Moeiro s/n, 4415-133 Pedroso, Portugal.

* ana.silva@fc.up.pt

Since the beginning of the 20th century plastic has been used as a raw material. PET bottles (polyethylene terephthalate) are one of the main types of plastics present in our environment and play a critical role in threatening the marine ecosystem because they persist in this environment for long periods of time, not being reused due to their contaminated and degraded state [1]. A sustainable and economically viable way to alleviate this problem is the recycling of these materials. It allows the reduction of existing waste, its reuse, and the production of new products for several areas. In the context of water analysis, it is possible to identify and quantify the presence of analytes of environmental importance through optical sensors that are devices precise, compact, and easy to transport.

This project aims to contribute to the reduction of PET plastics in marine ecosystems, through its transformation into materials capable of detecting and adsorbing pollutants in contaminated water. With this, we gave a new life to PET plastics collected from marine resources, by creating a kit of fluorescent sensors, from terephthalic acid obtained after the hydrolysis of PET (Figure 1). These sensors, when in contact with contaminated water, allow signaling by color change and/or fluorescence the presence of environmental contaminants, namely metal ions such as Fe(III) and Al(III), as well as adsorbing part of them [2, 3].

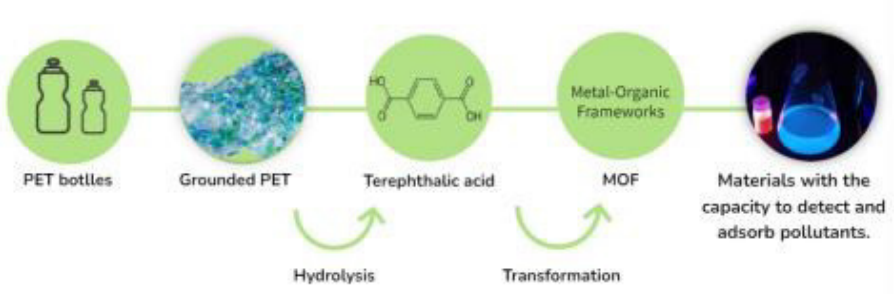


Figure 1: Sensor synthesis.

References
[1] K. Ghosal, C. Nayak, Mater. Adv. 3 (2022) 1974.
[2] B. Ruan, J. Yang, Y.-J. Zhang, N. Ma, D. Shi, T. Jiang, F.-C. Tsai, Talanta 218 (2020), 121207.
[3] T. Zhong, D. Li, C. Li, Z. Zhanga, G. Wang, Anal. Methods 14 (2022) 2714.

Funding: This work was financial supported with funding from FCT/MCTES (UIDP/50006/2020) through national funds.

Acknowledgments: This work received financial support from the project EXPL/QUI-OUT/1554/2021. We also thank National Funds (FCT/MCTES), under the Partnership Agreement PT2020 through projects NORTE-07-0162-FEDER-000048, UIDB/50006/2020 and UIDP/50006/2020. This project also counts with the partnership of Câmara Municipal de Ílhavo, through the Environmental Engineer, Luís Rabaça, and the Municipality Schools.

EXPLOITING THE NUTRITIONAL AND CHEMICAL DIVERSITY OF PORTUGUESE TOMATO (*SOLANUM LYCOPERSICUM* L.) GERMPLASM

Alexis Pereira,[1,2] Mikel Añibarro-Ortega,[1,2] Filomena Rocha,[3] Violeta Rolim Lopes,[3]
Ana Maria Carvalho,[1,2] Ana Maria Barata,[3] Lillian Barros,[1,2] José Pinela[1,2*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal. *jpinela@ipb.pt
[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]Banco Português de Germoplasma Vegetal (BPGV), Instituto Nacional de Investigação Agrária e Veterinária (INIAV), Quinta de S. José, S. Pedro de Merelim, 4700-859 Braga, Portugal.

Tomato (*Solanum lycopersicum* L.) is the second most important vegetable crop worldwide and one of the most preferred garden crops. It is a versatile key component of the Mediterranean diet commonly associated with a reduced risk of chronic degenerative diseases due to its composition in bioactive molecules [1,2]. Throughout its evolutionary and domestication process, this species has undergone diverse genetic and inbreeding phenomena that have led to the emergence of a vast number of varieties with different morphological and sensory attributes [3]. Many of these varieties have been grown by local farmers and represent a reservoir of genetic diversity with enormous potential for breeding and sustainable conservation. However, since information on tomato germplasm composition is limited, this study aimed to characterize the nutritional and chemical diversity of Portuguese table tomato genotypes. Tomato accessions (with the local names of “tomate comum”, “tomate coração-de-boi”, “tomate patinha”, “tomate cor-de-rosa”, and “tomate pera”) from the Portuguese Genebank collection were regenerated to obtain ripe fruits for replenish seeds and for analysis. After sample preparation, these were analyzed for their individual profiles of free sugars, organic acids, fatty acids, and tocopherols through different chromatographic techniques and carotenoids were quantified using a spectrophotometric method [1,4]. Furthermore, the proximate composition (moisture, protein, fat, and ash) was analyzed using AOAC procedures and carbohydrates were estimated by difference [1,4]. The characterized tomato table varieties showed differences in the contents of some investigated individual and crude constituents. The highest levels of carbohydrates, ascorbic acid, α- and β-tocopherol, monounsaturated fatty acids (MUFA), and polyunsaturated fatty acids (PUFA) and the lowest levels of crude fat, α- and γ-tocopherol, and saturated fatty acids (SFA) were detected in the so-called “tomate comum” accession. The “tomate pera” had the highest levels of free sugars, crude fat, SFA, and γ-tocopherol and the lowest levels of ascorbic acid and PUFA. On the other hand, the “tomate patinha” had the highest concentrations of protein and oxalic and citric acids, and the lowest glucose content. The “tomate cor-de-rosa” had the lowest concentrations of total carbohydrates, fructose, malic and citric acids, and carotenoids. In turn, the highest contents of malic acid and carotenoids and the lowest protein, oxalic acid, MUFA, and β-tocopherol contents were quantified in the “tomate coração-de-boi” accessions. Overall, these findings will be useful for establishing criteria for a rational selection of the most promising traditional table tomato varieties from a nutritional and chemical point of view. Their inclusion in sustainable food systems as tasty and healthy foods could contribute to the promotion of nutrition programs better adjusted to the consumers' preferences and dietary needs.

References

[1] J. Pinela, L. Barros, A.M. Carvalho, I.C.F.R. Ferreira, Food and Chemical Toxicology, 50 (2012) 829.
[2] J. Pinela, S.A. Petropoulos, L. Barros, Frontiers in Nutrition, 9 (2022) 1018498.
[3] B. Farinon, M.E. Picarella, F. Siligato, R. Rea, P. Taviani, A. Mazzucato, Frontiers in Plant Science, 13 (2022) 931233.
[4] J. Pinela, C. Montoya, V. Martins, et al., Scientia Horticulturae, 313 (2023) 111938.

Acknowledgments

The authors thank the Foundation for Science and Technology (FCT, Portugal) for the financial support through national funds FCT/MCTES to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); to FCT for the contracts of J. Pinela (CEECIND/01011/2018) and L. Barros (CEEC Institutional) and the PhD studentship granted to M. Añibarro-Ortega (2020.06297.BD). A. Pereira is grateful for his research grant to POSEUR-03-2215-FC000164 through the Sustainability and Efficiency in the Use of Resources program (POSEUR-15-2021-02) and Cohesion Fund.

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

POMEGRANATE LEAF EXTRACTS CHARACTERIZATION AND THEIR POTENTIAL USE AS A FUNCTIONAL INGREDIENT

Sandra Marcelino,[1,2,3] Filipa Mandim,[1,2] Taofiq Oludemi,[1,2,3] Sandrina A. Heleno,[1,2] Tiane C. Finimundy,[1,2]
Miguel A. Prieto,[3] 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] Universidade de Vigo, Nutrition and Bromatology Group, Department of Analytical Chemistry and Food Science, Faculty of Science, E-32004 Ourense, Spain
* lillian@ipb.pt

The pomegranate tree (*Punica granatum* L.) is indigenous to the Mediterranean region and is one of the oldest known plants. Studies have demonstrated their many biological and pharmaceutical benefits, which have been correlated to their bioactive content, namely secondary metabolites such as phenolic compounds [1]. However, 40 to 50% of the whole fruit is discarded, such as peel and leaves, originating valuable biowaste [2]. To support a circular economy and the prospective use of pomegranate biowaste as functional ingredients, the present research sought to ascertain the chemical composition and bioactive characteristics of pomegranate leaves. Maceration (ME), microwave (MAE), and ultrasound-assisted (UAE) extractions were the three extraction procedures chosen. HPLC-DAD-ESI/MS was used to identify and quantify the chemical composition of the various extracts. Two cell-based procedures were used to evaluate the antioxidant potential, TBARS and CAA. The antiproliferative potential was studied through sulforhodamine B colourimetric assays, using several tumour and a non-tumour cell lines. The extract's ability to reduce nitric oxide generation was used to determine its anti-inflammatory effects. Lastly, the microdilution technique was used to assess antimicrobial activity and cell viability assay conducted in two skin cell lines to support their possible use in topical formulation. According to the findings, the highest content of phenolic compounds was obtained in the MAE extract. Gallic acid, epicatechin, and granatin B were the most abundant compounds detected in all three extraction methodologies studied. All three extracts demonstrated lower IC_{50} values (0.83 - 1.70 μg/mL) than the positive control Trolox (IC_{50} = 9.1± 0.3 mg/mL), being the best results obtained for MAE and ME extracts. All extracts showed the capacity to halt the growth of tumour cell lines (GI_{50} between 19 and 76 μg/mL), being gastric adenocarcinoma (AGS), the cell line with the highest sensitivity. All three extracts demonstrated broad-spectrum antibacterial inhibition, in which *K. pneumoniae* displayed the highest sensitivity to the extracts (MIC values of 0.6 mg/mL). In the tested skin cell lines, none of the studied extracts had any observable adverse effects, and more than 50% of viability was maintained after exposure to the highest tested concentrations of each extract (400 μg/mL). According to our findings, pomegranate leaves appear to be a source of health-promoting biomolecules. Those results sustain their exploitation and possible use by food and pharmaceutical industries in some biobased products, enhancing the circular economy and zero biowastes.

References

[1] J. Xu, K. Cao. X. Liu, L. Zhao, Z. Feng, L. Liu, Antioxidants. 11 (2022) 29.
[2] R. R. Mphahlele, O. A. Fawole, N. P. Makunga, U. L. Opara, BMC Complementary Alternative Medicine. 16 (2016) 143.

Acknowledgments

To the Foundation for Science and Technology (FCT, Portugal) for financial support to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); PhD grant of Filipa Mandim (SFRH/146614/2019), L. Barros and S. Heleno contracts. Also, to FEDER for financial support through the project OliveBIOextract (NORTE-01-0247-FEDER-049865). This work is also supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891) and JDC contract of T. Oludemi (FJC2019-042549-I).

ALGAE BIOMASS AS PRECURSORS FOR PREPARATION OF MULTICOMPONENT LUMINESCENT SYSTEMS CONTAINING CARBON DOTS AND NATURAL PIGMENTS

Filipe M. Santos,[1*] Rui F. P. Pereira,[2] Bárbara M. C. Vaz,[3] Sónia P. M. Ventura,[3] Verónica de Zea Bermudez,[4] Sílvia C. Nunes[1]

[1] Chemistry Department and FibEnTech - Fiber Materials and Environmental Technologies, University of Beira Interior, Covilhã, Portugal; [2] Chemistry Department and Chemistry Centre, University of Minho, Braga, Portugal; [3] Department of Chemistry, CICECO—Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, Aveiro, Portugal [4]Department of Chemistry/CQ-VR, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal.
*filipe.miguel.santos@ubi.pt

Algae are rapidly becoming inspiring vehicles for innovation [1]. Besides their more traditional applications in the fields of human health and wellness, algae are gaining momentum in the preparation of new, sustainable and biocompatible materials, finding application in areas related with materials engineering, and energy [2, 3]. Algae possess a wide variety of phytochemicals of interest (*e.g.* proteins, pigments, polysaccharides) which, after being recovered, can be used in the preparation of materials with advanced functionalities. Among these are carbon dots (CDs), zero-dimensional, quasi-spherical nanoparticles with a carbon-based core. CDs have attracted considerable interest worldwide due to their excellent photoluminescence features, photostability, chemical inertness, environment-friendly nature, and low cost, which are anchored in facile synthetic procedures and great flexibility of surface modification. [4]

Although CDs usually emit in the UV/blue region of the spectra, they can also emit in other regions of the visible spectra with proper functionalization. By combining CDs with emission in the red, green and blue regions of the spectra, or even combining CDs with other types of phosphors, it is possible to assemble white light emitting devices, such as LEDs [5]. This, however, remains a challenge due to the wide variation of the properties between CDs and other phosphors, but also due to the need for stabilizing the latest against the different light-emitting CDs [5].

In this work, we report on the preliminary results regarding the optical properties of a system containing both CDs and a natural pigment. This system was naturally developed in an easy two-step process involving the extraction of the appropriate phytochemicals from the microalgae *Chlorella pyrenoidosa*, and the subsequent CD formation under microwave radiation, with an all-purpose solvent. The process allowed to obtain, in a single system, a blue / green / red phosphor. However, similar reactions with just the solvent or the same natural pigment solution failed to afford similar results, thus highlighting the importance of the algal precursor.

References

[1] M. Fabris, R.M. Abbriano, M. Pernice, et al., Front. Plant Sci. 11 (2020) 279.
[2] G.M. Elrayies, Renew. Sust. Energ. Rev., 81 (2018) 1175.
[3] F.G. Torres, G.E. de-la-Torre, Sustain. Energy Technol. Assess, 53 (2022) 102658.
[4] L. Đorđević, F. Arcudi, M. Cacioppo, M. Prato, Nat. Nanotechnol., 17 (2022) 112.
[5] Q. Han, W. Xu, C. Ji, et al., ACS Appl. Nano Mater., 5 (2022) 15914-15924.

Acknowledgments

This research was supported by National Funds from Foundation for Science and Technology (FCT) (PEST/QUI/00686/2020), SOLPOWINS (PTDC/CTM-REF/4304/2020), OBTAIN (NORTE-01-0145-FEDER-000084), and developed within the scope of the project Fiber Materials and Environmental Technologies (FibEnTech-UBI) (UIDB/00195/2020), financed by national funds through the FCT/MCTES (PIDDAC). R.F.P. Pereira acknowledges FCT/UMinho, for the contract in the scope of Decreto-Lei 57/2016–Lei 57/2017. S. C. Nunes acknowledges FCT for Assistant Research contract (2020-00805.CEEIND) in the scope of Scientific Employment Stimulus. F. M. Santos acknowledges the SOLPOWINS project for his Assistant Research contract. 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/MEC (PIDDAC).

IONIC LIQUIDS IN CONFINED SPACES

Artur F. M. Farinha*, Luís M. N. B. F. Santos, José C. S. Costa

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal. *up201506214@fc.up.pt

This study investigated the use of a customized procedure of thermal evaporation [1,2] to deposit ionic liquids (ILs) on surfaces with varying morphologies and physicochemical properties. The surfaces included organic semiconductor materials (OSCs) [3,4], indium-tin oxide (ITO), gold-coated quartz crystals, and nanoporous anodic aluminum oxide (AAO) membranes. An argon plasma treatment was used to manipulate the positioning and morphology of the ILs. The study compared the effect of the alkyl chain length of imidazolium-based ILs [5,6], and found that longer chains had greater affinity with OSCs. For the gold-coated quartz crystal microbalance, the research found that the ILs moved into confined spaces and formed droplets on the surface once these spaces were filled, rendering the balance non-functional [7,8]. The positively charged AAO membranes exhibited good affinity with the ILs, through its anion. Larger pore sizes hindered the confinement of the ILs, leading to a continuous film over the unfilled pores. This was attributed to the increased area between adjacent pores, rather than the pore size itself. Overall, these findings provided insights into the dynamics of ILs on both porous and non-porous surfaces. This knowledge could be useful for engineering nanostructures consisting of ILs in nanoconfined spaces.

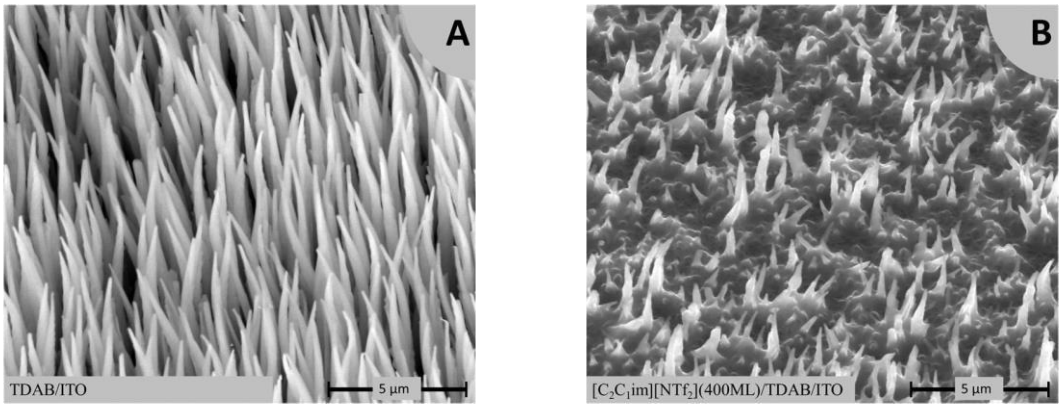


Figure 1: SEM images depicting the film morphology of the organic semiconductor 1,3,5-tris(diphenylamino)benzene (TDAB), both without (A) and with (B) the confinement of an ionic liquid.

References

[1] J.C.S. Costa, R.M. Rocha, I.C.M. Vaz, M.C. Torres, A. Mendes, L.M.N.B.F. Santos, J. Chem. Eng. Data, 60 (2015) 3776-3791.
[2] J.C.S. Costa, A.F.S.M.G. Coelho, A. Mendes, L.M.N.B.F. Santos, Appl. Surf. Sci., 428 (2018) 42-249.
[3] J.C.S. Costa, M.A. Lima, A. Mendes, L.M.N.B.F. Santos, RSC Adv., 10 (2020) 11766.
[4] J.C.S. Costa, R.J.S. Taveira, C.F.R.A.C. Lima, A. Mendes, L.M.N.B.F. Santos, Opt. Mater., 58 (2016) 51-60.
[5] J.C.S. Costa, A. Alves, M. Bastos, L.M.N.B.F. Santos, Phys. Chem. Chem. Phys., 24 (2022) 13343-13355.
[6] J.C.S. Costa, R.M. Campos, A.C.M. Castro, A.F.M. Farinha, G.N.P. Oliveira, J.P. Araújo, L.M.N.B.F. Santos, CrystEngComm., 25 (2023) 913-924.
[7] L.M.N.B.F. Santos, A.I.M.C. Lobo Ferreira, V. Štejfa, A.S.M.C. Rodrigues, M.A.A. Rocha, M.C. Torres, F.M.S. Tavares, F.S. Carpinteiro, J. Chem. Thermodyn., 126 (2018) 171-186.
[8] F. Borghi, A. Podestà, Adv. Phys.: X, 5 (2020) 1736949.

Acknowledgments

The authors thank the Portuguese Foundation for Science and Technology (FCT) for financial support to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020), Faculty of Science, University of Porto. A.F.M. Farinha also thanks the FCT for the award of a Ph.D. Research Grant (ref. 2022.11342.BD).

FLASH COMMUNICATION

MICROPARTICLES CONTAINING ACTINIDIA ARGUTA EXTRACTS PREPARED BY SPRAY DRYING

Filipa Teixeira[1], Ana Margarida Silva[1], Cristina Delerue-Matos[1], Berta Estevinho[2,3], Paulo C. Costa [4,5], Francisca Rodrigues[1,*]

[1]REQUIMTE/LAQV, ISEP, Polytechnic of Porto, Porto, Portugal; [2]LEPABE, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal; [3]ALiCE—Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal; [4]REQUIMTE/UCIBIO, MedTech-Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal; [5]Associate Laboratory i4HB—Institute for Health and Bioeconomy, Faculty of Pharmacy, University of Porto, Porto, Portugal.
*francisca.rodrigues@graq.isep.ipp.pt

Actinidia arguta is a perennial vine rich in phenolic compounds with outstanding therapeutic properties [1]. Along with kiwiberries (KB), different *A. arguta* by-products, particularly leaves, have been highlighted for their incredible polyphenolic content. However, polyphenols are extremely sensitive, being necessary to develop suitable delivery systems, such as microparticles, to provide protection and control release. This study aims to produce, by spray-drying, microparticles of KB and *A. arguta* leaves (AAL) extracts and compare them regarding size, shape, antioxidant/antiradical activities, swelling capacity, moisture content, and effect on cells viability (TR146 and HSC-3). KB extract was prepared according to Macedo *et al.* [1], while the AAL extract was obtained following the methodology described by Silva *et al.* [2]. Different microparticles were prepared: empty microparticles (RS30DM) only composed by the encapsulating agent (Eudragit RS 30 D (1%)), KB extract microparticles (KBM) and AAL extract microparticles (AALM) [3]. The microparticles shape was investigated through scanning electron microscopy (SEM), showing a spherical morphology like a biconcave disc. The size, swelling capacity, moisture content and antioxidant/antiradical activities of all microparticles are described in Table 1. The KBM did not show significant differences ($p>0.05$) when compared to the empty microparticles, while AALM achieved a significant high antioxidant and antiradical activities.

Table 1: Size, moisture content, swelling capacity and antiradical/antioxidant activities of all microparticles evaluated by DPPH and FRAP assays. Results are expressed as mean ± standard deviation ($n = 3$). Different letters in the same column mean significant differences ($p < 0.05$).

Microparticles	Size (µm)	Moisture content (%)	Swelling capacity (%)	FRAP (µmol FSE/g)	DPPH (mg TE/g)
RS30DM	0.31 - 5.95	4.48 ± 1.70 ^{b}	17.20 ± 3.36 ^{a}	28.43 ± 3.72 ^{a}	2.48 ± 0.40 ^{a}
KBM	0.33 - 8.62	16.93 ± 2.55 ^{a}	4.98 ± 0.35 ^{b}	30.30 ± 3.21 ^{a}	2.15 ± 0.27 ^{a}
AALM	1.85 - 6.33	7.34 ± 0.47 ^{b}	12.34 ± 1.82 ^{a,b}	81.72 ± 4.31 ^{b}	4.90 ± 0.60 ^{b}

The *in vitro* cell assays demonstrated that microparticles did not lead to a viability decrease on both cell lines between 62.5 and 1000 µg/mL. The results suggest that AALM are the most promising microparticles. LC-MS analysis should be performed to assess the encapsulation efficiency, along with studies regarding the *in vitro* controlled release in order to evaluate the release of bioactive compounds over time.

References

[1] Macedo, C., et al., Scientia Horticulturae, 313 (2023) 111910; [2] Silva, A. M., et al., Industrial Crops and Products 184 (2022) 115090; [3] Ribeiro, A. M, Estevinho, B. N., Rocha, F., Food and Bioprocess Technology 12 (2019) 1381-1394.

Acknowledgments

This work received financial support from project EXPL/BAA-GR/0663/2021 – Kiwi4Health – Exploring the Eco-Innovative Re-Use of Kiwiberry, supported by national funds by FCT/MCTES and by the projects UIDB/50006/2020 and UIDP/50006/2020 through national funds as well as UIDP/04378/2020, UIDB/04378/2020 and the project LA/P/0140/2020. Filipa Teixeira is thankful for the scholarship from project EXPL/BAA-GR/0663/2021. Ana Margarida Silva is thankful for the Ph.D. grant (SFRH/BD/144994/2019) financed by POPH-QREN and subsidized by the European Science Foundation and Ministério da Ciência, Tecnologia e Ensino Superior. Francisca Rodrigues (CEECIND/01886/2020) is thankful for contract financed by FCT/MCTES—CEEC Individual Program Contract. This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); Also, Berta Estevinho acknowledges FCT for the contract based on the "Lei do Emprego Científico" (DL 57/2016 – norma transitória).

FIG (*FICUS CARICA* L.) BIORESIDUES AS A SOURCE OF BIOACTIVE COMPOUNDS: A SUSTAINABLE APPROACH

Carlos S. H. Shiraishi[1,2,3], Yosra Zbiss,[1,2], Custódio Lobo Roriz[1,2], Maria Inês Dias[1,2], Márcio Carocho[1,2], Ricardo C. Calhelha[1,2], Maria José Alves[1,2], Vasco da Cunha Mendes[4], Rui M. V. Abreu[1,2], Miguel A. Prieto[3], Sandrina A. Heleno[1,2] and Lillian Barros[1,2*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Alameda Santa Apolónia 5300-253, 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]Nutrition and Bromatology Group, Universidad de Vigo, Depart of Analytical Chemistry and Food Science, Faculty of Science, E-32004 Ourense, Spain;
[4]Sociedade Agrícola Quinta da Mó de Cima, S.A., Rua Julieta Ferrão, 12 Torre A 602, 1600 – 131 Lisboa, Portugal;
* lillian@ipb.pt

Fig production bioresidues can be used as a source of bioactive compounds that can be transformed into value-added products of industrial interest. This sustainable approach can reduce waste, environmental pollution and add value to the agricultural chain, besides having a positive and sustainable economic impact [1]. To identify the most promising varieties that produce significant amounts of bioresidues (leaves and fruit) aiming to recover bioactive molecules based on the 2030 goals, the current research was designed to study and understand the chemical profile from the leaves and fruits of five fig varieties (Dauphine - Da, Longue d'Aout - La, Pasteliere - Pa, Marseille - Ma, and Bourjassote Noire - Bn).

The results were obtained resorting to different chromatographic techniques for the identification of the different compounds (organic acids, phenolic compounds, tocopherols, fatty acids, and free sugars), and showed that in each fig variety, weather it is the leaves or the fruits, a distinct chemical profile is observed, allowing to highlight the most promising varieties. For organic acids, Bn presented the highest amount of these compounds in the leaves (146.5±1.1 mg/g dw) and fruits (34.25±0.31 mg/g dw). In terms of phenolic composition, La leaves and Bn fruits presented the best profile of phenolic compounds(42.4±0.2 mg/g dw, and 2.897 ± 0.001 mg/g dw, respectively). For tocopherols, Pa leaves (4.14±0.05 mg/g dw) and Ma fruits (2.4±0.03 mg/g dw) were the ones that stood out. Regarding the free sugars, Da was the most promising variety for leaves (17.36±0. 08 mg/g dw) and fruits (87.78±0.77 mg/g dw). Concerning the fatty acids, polyunsaturated ones (PUFA) were predominant in leaves ranging from 53% (Ma) to 71% (La) of total fatty acids, while in the fruit the range was from 40% (La) to 47% (Ma). Even though both fruits and leaves had different chemical profiles, it is relevant to state that leaves were found to be a greater source of chemical compounds than fruits, particularly leaves of Bn and Da, which may have high potential to be included in formulations from different industrial sectors such as the food, cosmetics, and pharmaceutical industries.

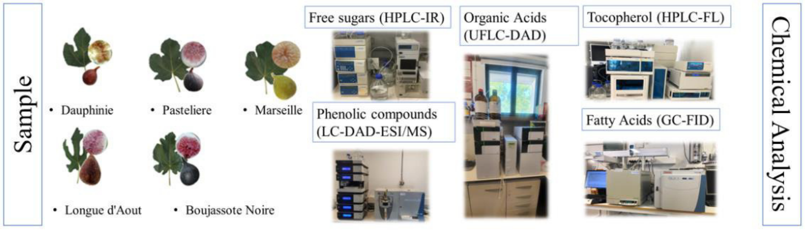


Figure 1: Bioresidues and chromatographic analysis for identification of chemical profile

References

[1] AYUSO, Manuel, et al.. Trends in Food Science & Technology, 2022.

Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES to the CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021). M. Carocho thanks FCT for his individual employment program–contract (CEEC-IND/00831/2018), and L. Barros, R. Calhelha, M.I. Dias and S. Heleno also thank to the national funding by FCT through the institutional scientific employment program–contract. the European Regional Development Fund (ERDF) through the Competitiveness and Internationalization Operational Program for financial support to the project 100% Figo (POCI- 01-0247- FEDER-064977) and for C. Shirashi and C. L. Roriz PhD and Post-Doc grants, respectively.

EFFICIENCY OF CHEMICAL PRECIPITATION TECHNIQUE IN THE REMOVAL OF ORGANIC MATTER FROM INDUSTRIAL EFFLUENT OF SLAUGHTERHOUSE

Karina S. Silvério,[1*] Margarida Oliveira,[1,2] Fátima Carvalho[2,3,4]; Adelaide Almeida,[2,3,4]

[1] Department of Technology and Applied Sciences, School of Agriculture, Polytechnic Institute of Beja, 7800-295, Beja, Portugal; [2] Department of Chemistry, University of Beira Interior, 6201-001 Covilhã, Portugal; [3] FibEnTech/UBI Research Unit, University of Beira Interior, 6201-001 Covilhã, Portugal.; [4] CENSE - Center for Environmental and Sustainability Research, Faculty of Science and Technology, University Nova de Lisboa, 2829-516 Caparica, Portugal.
*karina.biotecnologia@hotmail.com.

The impacts caused by anthropogenic actions on the aquatic environment have been one of the main challenges of modern society. The increasing urbanization combined with population growth induces a permanent increase in water demand and, consequently, the need to improve the resilience of production systems through more efficient treatment technologies. Based on the circularity context, the study developed had to evaluate how the raw effluent composition interferes in the efficiency of the Chemical Precipitation Process (CPP), using hydrated lime ($Ca(OH)_2$) as reagent in wastewater from the agro-industrial sector, namely wastewater from slaughterhouses. For this study five samples of slaughterhouse effluents were collected throughout the year. For each collection the following methodology was applied: 1) Application of the reagent in a single step, raising the pH to 12.5 [1]. 2) Obtaining the treated sludge and effluents. 3) Natural neutralization of the effluent by carbonation using atmospheric CO_2 [2]. 4) Physicochemical characterization and evaluation of the feasibility of the chemical precipitation technique of the slaughterhouse effluent. The results showed an average phosphorus removal efficiency of 99% ±0.01 for the five collections. Regarding the removal of organic matter varied according to each collection and showed different removal efficiencies being the highest efficiency for the water containing the highest percentage of organic matter, about 91% ±0.3. Figure 1 presents the appearance of color before and after the treatment of the slaughterhouse effluent.

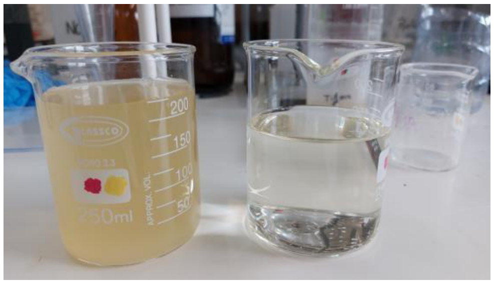


Figure 1 - Slaughterhouse effluent before and after application of the chemical precipitation technique

References:

[1] L. Madeira; A. Almeida; M. R. Teixeira; A. Prazeres; H. Chaves; F. Carvalho., Immediate one-step lime precipitation and atmospheric carbonation as pre-treatment for low biodegradable and high nitrogen wastewaters: A case study of explosives industry, J. Environ. Chem. Eng. 8 (2020), 103808.
[2] L. Madeira; F. Carvalho.; A. Almeida; M. R. Teixeira. Optimization of atmospheric carbonation in the integrated treatment immediate one-step lime precipitation and atmospheric carbonation. The case study of slaughterhouse effluents. Results in Engineering 17 (2023), 100807.

Acknowledgmets

This work was developed under the NETA project - New Strategies in Effluent Treatment (POCI-01-0247-FEDER-046959) funded by PORTUGAL2020. The Fundação de Ciência e Tecnologia FCT for awarding the research grant to Karina Santos Silvério.

PHARMACEUTICALS' MIXTURES: EVALUATION OF ITS ELECTROCHEMICAL QUALITATIVE SEPARATION

A. R. Queijo,[1*] H. Teixeira,[1] R. Rego[2]

[1]CQ-VR, School of Life and Environmental Sciences, University of Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801 Vila Real, Portugal; [2] Chemistry Department and CQ-VR, School of Life and Environmental Sciences, University of Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801 Vila Real, Portugal
*anaritaqueijo@gmail.com; rrego@utad.pt

In the last decade, pharmaceuticals have emerged as a new class of environmental micropollutants, as they can lead to ecological and public health problems [1].

Recently, drugs' electrochemical methods have been developed [2,3]. Evaluation of the peak current as a function of concentration (in triplicate) at different analyte concentrations was used to obtain the drugs' analytical curves.

Validation parameters were calculated from the calibration curves, such as linear equation (slope and intercept), regression coefficient, limits of detection and quantification.

Since several pharmaceuticals can coexist in river water, we decided to make different mixtures to evaluate the possibility of their qualitative separation. The mixtures in study will be carbamazepine (CBZ) + paracetamol (PAR), PAR + naproxen (NPX) and CBZ + PAR + NPX.

The objectives of this work will be to analyse the binary and ternary mixtures (**Figure 1**) and to evaluate the possibility of qualitative separation of drugs. The analysis will be performed on the glassy carbon electrode (GCE - Metrohm RDE.GC50 80392), using differential pulse voltammetry.

Future work should focus on the testing of these mixtures with the IoT device (through machine learning training) currently being improved in the Engineering Department of University of Trás-os-Montes e Alto Douro. Previously, we have already described the application of an IoT device for analyses of ferrocyanide as a model compound with promising results [3].

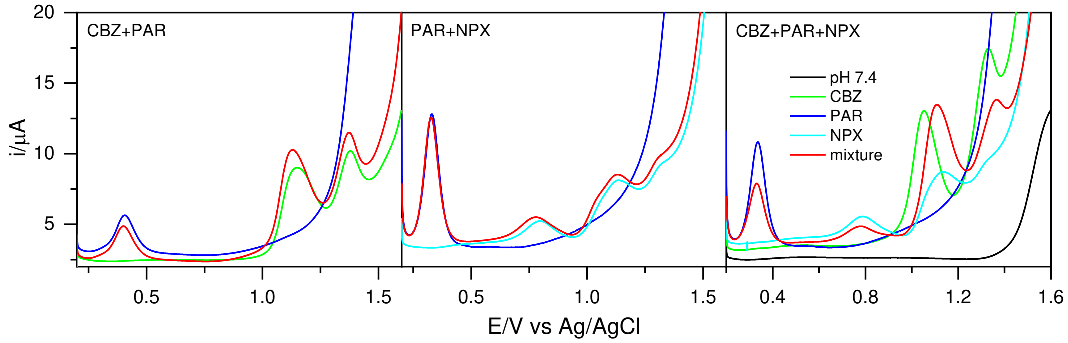


Figure 1: Curves of CBZ + PAR, PAR + NPX and CBZ + PAR + NPX mixtures.

References

[1] M. I. López-Cázares, E. D. Isaacs-Páez, J. Ascacio-Valdés, C. N. Aguilar-González, J. R. Rangel-Mendez, and L. F. Chazaro-Ruiz, *Sep. Purif. Technol.*, 258 (2020) 118030.

[2] W. Fins, A. M. Ferraria, A. M. Botelho do Rego, A. Valente, C. Antunes, R. Rego, Symposium 2, The 70th Annual Meeting of the International Society of Electrochemistry, Durban, South Africa, 4-9 August 2019.

[3] R. Rego, W. Fins, F. Barreira, C. Antunes, A. Valente, Symposium 1, The 72th Annual Meeting of the International Society of Electrochemistry, on-line, 29 August-3 September 2021.

Acknowledgments

This work was supported by OBTAIN (Objective Building Sustainability) I&D project NORTE-01-0145-FEDER-000084, 2021-2023, co-financed by FEDER (Fundo Europeu de Desenvolvimento Regional) through NORTE 2020 (Programa Operacional Regional do Norte 2014/2020). A. R. Queijo thanks BI/UTAD/28/2022.

TREATMENT OF AGRO-INDUSTRIAL WASTEWATER: BATCH VS CONTINUOUS SYSTEM

Nuno Jorge,[1,2*] Ana R. Teixeira,[2] Ana Gomes,[2] Marco S. Lucas,[2] 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, 5001-801, Vila Real, Portugal.
*njorge@uvigo.es

In this work, three agro-industrial wastewaters resulting from the production of wine (red and white) and olive oil were treated by Fenton-based processes. The aim and novelty of this work was the comparison of batch versus continuous reactors, using nitriloacetic acid (NTA) to prevent the precipitation of iron. Initially, different processes (H_2O_2, UV-C, UV-C + Fe^{2+}, UV-C + H_2O_2, Fenton and photo-Fenton) were studied in batch mode, to treat a red wine wastewater (WW), with results showing high dissolved organic carbon (DOC) removal by the photo-Fenton process (79.7%). The photo-Fenton process efficiency was shown to be dependent of factors such as the pH, H_2O_2 and Fe^{2+} concentrations (Figure 1). To enhance DOC removal and prevent Fe^{2+} precipitation, NTA was applied in different concentrations. Results showed two pseudo first-order kinetic regimes, one from 0 to 1.0 mM NTA with a slope of 0.00378 mM min^{-1} (the kinetic constant in directly proportional to the amount of NTA) and another from 2.5 to 10.0 mM with a slope of 0.00069 mM min^{-1} (kinetic constant decreases linearly with the concentration of NTA). Therefore, under the best conditions (pH = 3.0, $[H_2O_2]$ = 194 mM, $[Fe^{2+}]$ = 1.0 mM, [NTA] = 1.0 mM, radiation UV-C (254 nm), time = 240 min), it was observed an electric energy per mass (E_{EM}) of 0.494, 0.519 and 0.496 kWh.g DOC^{-1} and a cost of 0.0421, 0.0439 and 0.0421 €/g DOC/L, respectively for red WW, white WW and olive mill wastewater (OMW). The next phase of the work consisted in the application of the best operational conditions in a continuous mode, using a peristaltic pump to add the wastewater + H_2O_2 to the reactor. Initially, it was tested different H_2O_2 concentrations (24.3 to 242.5 mM), with results showing high DOC removal with 97 mM (93.6%). This H_2O_2 concentration was applied in different flow rates (1 – 15 mL min^{-1}), with results showing lower E_{EM} (0.379 kWh.g DOC^{-1}) with F = 3 mL min^{-1}). Finally, the continuous system was applied to different agro-industrial wastewaters, with results showing a cost of 0.032, 0.032 and 0.030 €/ g/L DOC, respectively. Based in the results, NTA-photo-Fenton shows an efficient reduction of the organic matter from the agro-industrial wastewaters studied. The continuous systems have high capacity for removal of organic matter and can be adapted for industrial scale. Finally, it can be concluded that NTA-photo-Fenton is efficient for the removal of phenolic compounds, reducing the toxicity of the wastewater.

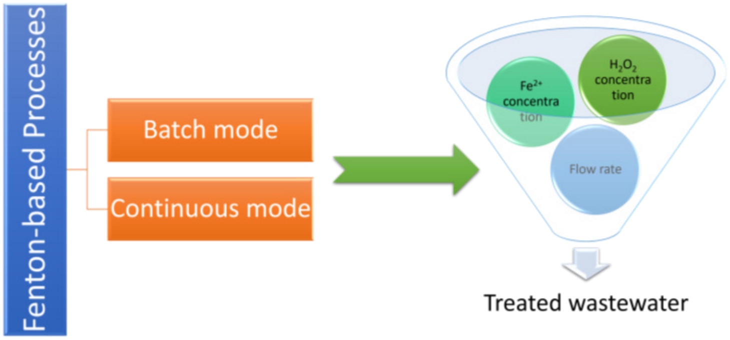


Figure 1: Fenton-based processes applied for agro-industrial wastewater treatment.

Acknowledgments
The authors are grateful for the financial support of the Project AgriFood XXI, operation No. NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to CQVR through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

A COMPUTATIONAL STUDY ON THE HYDROSILYLATION OF IMINES

Edgar Silva-Santos,[1,*] Filipe Teixeira,[2] Anthony J. Burke[3,4,5], M. Natália D. S. Cordeiro,[1]

[1]LAQV-REQUIMTE, Faculty of Sciences of University of Porto, Porto, Portugal
[2]Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[3]Faculty of Pharmacy, University of Coimbra, Pólo das Ciências da Saúde, 3000-548 Coimbra, Portugal
[4]LAQV-REQUIMTE, IIFA, University of Évora, 7000 Évora, Portugal
[5]Centro de Química de Coimbra, Institute of Molecular Sciences, Faculty of Sciences and Technology, Coimbra, Portugal

Hydrosilylation reactions have been extensively used in the enantiomeric reduction of imines due to their economic advantages in the utilization of inexpensive reagents. [1,2]. While metallic catalysts were primarily used for this reaction, organocatalysts have recently emerged as a promising alternative that provides similar or better results [3]. Specifically, picolinamide-cinchona organocatalysts have been demonstrated to have a high enantioselectivity of up to 91% ee and a high turnover frequency when paired with trichlorosilane [4]. In this study, we aimed to elucidate the mechanism of hydrosilylation reactions using these organocatalysts, through well-established DFT methods (GGA functional B97 with D3 dispersion correction and def2 with triple-zeta valence basis set). Both the energy profiles of the intermediates and transition states involved in the reaction as well as the limiting step were determined. Our findings further revealed that the proposed mechanism of the hydrosilylation reaction using picolinamide-cinchona catalysts was similar to the one originally proposed by Matsumura and co-workers [5]. Furthermore, they provide a better understanding of the factors that govern the selectivity and efficiency of the reaction. Such knowledge is crucial for developing new and more efficient catalytic systems. Therefore, our study has significant implications for the field of organocatalysis, particularly in imine reductions.

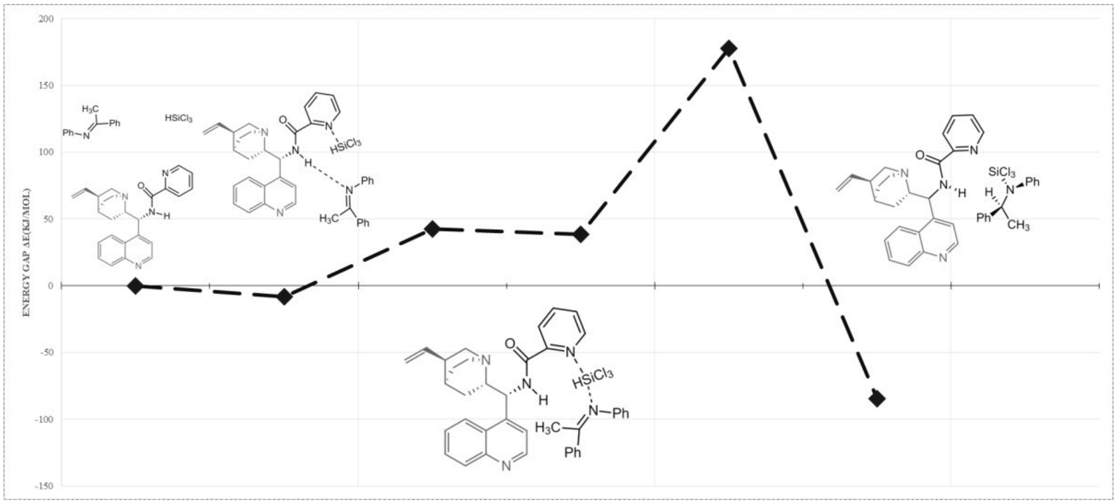


Figure 1: Reaction energy profile.

References
[1] N. Fleury-Brégeot, V. de le Fuente, S. Castillón, C. Claver, ChemCatChem 2 (2010) 1346.
[2] T. C. Nugent, M. El-Shazly, Adv. Synth. Catal. 352 (2010) 753
[3] S. Jones, C. J. A. Warner, Org. Biomol. Chem. 10 (2012) 2189.
[4] P.C. Barrulas, A. Genoni, M. Bengalia, Eur. J. Org. Chem. 33 (2014) 7339
[5] F. Iwasaki, O. Onomura, K. Mishima, T. Kanematsu, T. Maki, Y. Matsumura, Tetrahedron Letters 42 (2001) 2525

Acknowledgments
This work was supported by FCT/MCTES through national funds and co-financed by FEDER (Project UIDB/5006/2020). The author further acknowledges FCT/MEC for the funding of a doctoral grant.

PHENOLIC COMPOSITION AND *IN VITRO* BIOACTIVITIES OF CARDOON BLADES: STUDY OF ITS POTENTIAL AS A FUNCTIONAL INGREDIENT

Filipa Mandim,[1,2,3] Spyridon A. Petropoulos,[4] José Pinela,[1,2] Maria Inês Dias,[1,2] Isabel C.F.R. Ferreira,[1] Celestino Santos-Buelga,[3] 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, Campus Miguel de Unamuno, 37007 Salamanca, Spain; [4]University of Thessaly, Department of Agriculture, Crop Production and Rural Environment, 38446, Volos, Greece. *lillian@ipb.pt

Cynara cardunculus L. var. *altilis* DC., commonly known as cardoon, belongs to the Asteraceae family. This species is integrated into the Mediterranean diet and also has several industrial applications (e.g., pharmaceutical, cosmetic, energetic, paper pulp, and food industries) [1]. Over the last decade, cardoon has been attracting high interest from several industrial sectors. In addition to low requirements in agronomic inputs and high adaptation to adverse environmental conditions, cardoon exhibits a high concentration of bioactive compounds as well as biomass yields [1,2]. Despite the multifaceted applications of cardoon, vegetable tissues such as blades and floral stems are commonly discarded and consequently considered biowaste [1,3]. The adequate exploitation and characterization of the species are essential for circular economic stimulation and environmental impact reduction. Cardoon blades were collected in Greece at sixteen maturation stages (B1-B16). Phenolic composition and several *in vitro* bioactive properties of their hydroethanolic extracts were studied. The polyphenolic profile was analyzed by HPLC-DAD-ESI/MS. The antioxidant potential was studied through two cell-based assays: TBARS and OxHLIA. The anti-inflammatory activity was evaluated through the extracts' capacity to inhibit the formation of the pro-inflammatory mediator nitric oxide. Finally, the antiproliferative potential was evaluated against four tumors and a non-tumor cell line (PLP2) using the sulforhodamine B colorimetric assay. Twenty phenolic compounds were tentatively identified. 5-*O*-Caffeoylquinic acid, *trans* 3,4-*O*-dicaffeoylquinic acid, and luteolin-*O*-hexoside were the compounds found in higher concentrations. Immature blades (B3) exhibited the highest phenolic content (178 mg/g extract) and capacity to inhibit the thiobarbituric acid reactive substances formation (IC_{50} = 1.61 μg/mL). On the other hand, samples at more advanced stages of maturation exhibited higher antiproliferative (B8–B13, GI_{50} between 7 and 17 μg/mL) and anti-inflammatory activities (B13, IC_{50} of 10 μg/mL), as well as higher capacity to inhibit oxidative hemolysis (B8, IC_{50} = 25 and 47 μg/mL for Δt of 60 and 120 min, respectively). This study proved that the maturity stage influences the phenolic composition and bioactive potential of cardoon blades which could be valorized as a functional ingredient for food and pharmaceutical applications.

References

[1] F. Mandim, S.A. Petropoulos, J. Pinela, et al., Biology, 11 (2022), 699.
[2] A. Ierna, O. Sortino, G. Mauromicale, et al., Agronomy, 10 (2020), 1548.
[3] A. Cabiddu, S. Contini, A. Gallo, et al., Industrial Crops and Products, 130 (2019), 420.

Acknowledgments

To the Foundation for Science and Technology (FCT, Portugal) for financial support to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); PhD grant of Filipa Mandim (SFRH/146614/2019) and J. Pinela (CEECIND/01011/2018), M.I. Dias and L. Barros contracts.

SYNTHESIS AND CHARACTERIZATION OF MONOLITH SILICA/FIBER AEROGEL FOR WATER ADSORPTION

T.L.Silva[1,2]*, C.Dariva[1], J.F.De Conto[1], L.Durães[2], S.M.Egues[1]

[1] Postgraduate Program in Process Engineering (PEP)/Laboratory of Materials Synthesis and Chromatography (LSINCROM),
Center for Studies in Colloidal Systems (NUESC)/Institute of Technology and Research (ITP)/Tiradentes University (UNIT),
Av. Murilo Dantas, 300, Aracaju, SE CEP 49032-490, Brazil
[2] University of Coimbra, CIEPQPF, Department of Chemical Engineering, 3030–790 Coimbra, Portugal
*thauane.silva@uc.pt

The presence of high water content in the flow of natural gas (NG) from the exploration of wells located in the pre-salt region requires the development of technologies capable of minimizing the risks caused by the formation of hydrates, teasing corrosion in the pipes, and clogging in the lines. In this way, the dehydration of NG by the adsorption process through solid desiccants is an interesting alternative because it allows the use of new materials, such as the use of silica, which presents high thermal and physical-chemical stability. [1]. However, despite having unique properties, pure silica aerogels generally exhibit brittle behavior in some large-scale applications. Therefore, to overcome this drawback, aerogels derived from tetraethoxysilane/vinyltrimethoxysilane (TEOS/VTMS) reinforced with eucalyptus pulp were synthesized and dried by freeze-drying. In this work, monoliths were synthesized in cylindrical formats with a low density of approximately 0.18 g/cm^3, which is an advantage, as it reduces the weight of ships and thus promotes energy savings. FTIR analysis confirmed the hydrophilicity of the material, showing a broad absorbance band in the region of 3000–3600 cm^{-1} corresponding to the O–H elongation including bound Si–OH. The band at 2920 cm^{-1} is related to amino groups introduced on the silica surfaces, confirming the material modification. The band in the region 1054 cm^{-1} and 790 cm^{-1} confirms the Si–O-Si vibrations. Therefore, it is noteworthy that the silica/fiber monolith shows unique properties for water adsorption, having both organic and inorganic properties, such as good permeability, selectivity, chemical stability, and thermal and mechanical resistance [2].

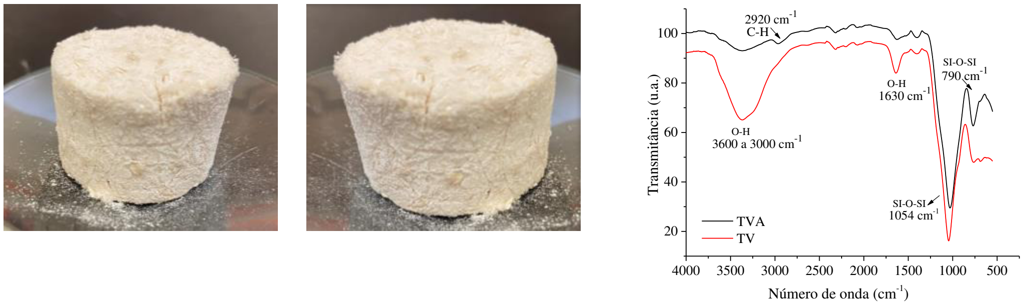


Figure 1: Monolith reinforced with silica fibers.

References

[1] Kátilla M. C. Santos, Tamires R. Menezes, Marília R. Oliveira, Thauane S. L. Silva, Klebson S. Santos, Vinicius A. Barros, Darley C. Melo, André L. Ramos, Cesar C. Santana, Elton Franceschi, Cláudio Dariva, Silvia M. Egues, Gustavo R. Borges, Juliana F. De Conto, Chemical Engineering Journal, 2021.
[2] Rafael B. T, João P. V, Alyne L-M, Luísa D, The Journal of Supercritical Fluids, 147 (2019) 81–89.

Acknowledgments

The authors thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Higher Education Personnel Improvement Coordination, Brazil, CAPES - financing code 001) for financial support. The authors would like to thank the Department of Chemical Engineering (Universidad de Coimbra) for the analysis and were also for financing Innovation.

GOLD TRIS-BINOL MENTHOL MONOPHOSPHITE FOR THE PREPARATION OF PHENOL DERIVATIVES

Zoe A. Arnaut,[1] Alexandre P. Felgueiras,[1] Philipp M. Stein,[2] Matthias Rudolph,[2] Sónia A. C. Carabineiro,[3] Rui M. B. Carrilho,[1] A. Stephen K. Hashmi,[2] Mariette M. Pereira[1]*

[1]Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal; [2]LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade NOVA de Lisboa, Caparica 2829-516, Portugal; [3]Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.
*mmpereira@qui.uc.pt

Bulky phosphites form stable complexes with gold, which can be used as catalysts in the Hashmi phenol synthesis.[1] For a long time, organic chemists overlooked gold catalysis. However, in the past few years, the field of homogeneous gold catalysis for organic reactions has grown rapidly.[2] Gold catalysts can selectively react and produce highly complex molecules. Gold complexes can coordinate with C-C bonds and interact with the π-system and activate it for nucleophilic attack. In recent years, homogeneous gold catalysis has received considerable attention for activating and functionalizing alkynes.[3] The diamagnetic character of both gold(I) and gold (III) conveniently allows the monitoring of the catalytic reactions by NMR.[2]

In this presentation, we show the synthesis of a chiral tris-BINOL-menthol derivative and its complexation with gold (I) (Figure 1) which was obtained with yields up to 91%. Application in gold-catalysed phenol synthesis and kinetic studies will be discussed.

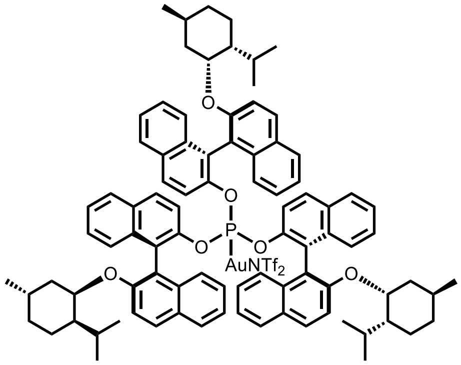


Figure 1: Tris-BINOL-menthol phosphite gold (I) complex.

References
[1] M. C. Blanco Jaimes, F. Rominger, M. M. Pereira, R. M. B. Carrilho, S. A. C. Carabineiro, A. S. K. Hashmi, Chemical Communications, 50 (2014) 4937
[2] A. S. K. Hashmi, Chemical Reviews, 107 (2007) 3180
[3] C. H. Leung, M. Baron, A. Biffis, Catalysts, 10 (2020) 1

Acknowledgments
The authors thank FCT for the funding of the bilateral project DAAD-Alemanha 5625-DRI-DAAD-2020/21.

SYNTHESIS AND BIOLOGICAL ACTIVITY OF NEW BISQUINOLIZIDINE DERIVATIVES FROM BIO RENEWABLE RESOURCES

Daniela R. Ferreira,[1*] Raquel M. Durão,[1] Ana Margarida M. M. Fernandes,[1] Carlos A. M. Afonso,[1] Jaime A. S. Coelho[2]

[1] Research Institute for Medicines, Faculty of Pharmacy, University of Lisbon, Avenida Professor Gama Pinto 1649-003 Lisbon, Portugal; [2] Centro de Química Estrutural, Institute of Molecular Sciences, Faculty of Sciences, University of Lisbon, Campo Grande, 1749-016 Lisbon, Portugal.
*ferreira-daniela@edu.ulisboa.pt

Bisquinolizidine alkaloids, such as (-)-sparteine and (+)-lupanine, are found in several plants of the subfamily Faboideae including the genus *Lupinus*. These molecules are characterized by a common chiral bispidine core [1] and possess a variety of biological activities, (-)-sparteine has both antiarrhythmic [2,3] and anticonvulsant properties and (+)-lupanine is moderately toxic [4]. Our group have been developing methods for the sustainable isolation of these alkaloids [5]. Currently, our research interests include developing methodologies for the functionalization of bisquinolizidine alkaloids for medicinal chemistry applications. In this work, we present two synthetic strategies: a) synthesis of 17-substituted lupanine derivatives through the nucleophilic addition of Grignard reagents to the iminium ion derived from lupanine (**Figure 1a**); and b) synthesis of ammonium salts through N-alkylation reactions (**Figure 1b**). Finally, we present preliminary results of the biological activity of these bisquinolizidine derivatives.

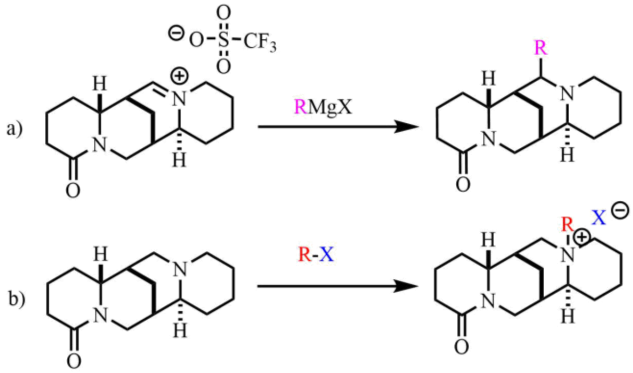


Figure 1: Reaction scheme of the addition of Grignard reagents (a) and alkylation reactions (b).

References

[1] J. Goller, C. Hübschle, M. Breuning, European J Org Chem, 5 (2019) 895.
[2] J. Senges, L. Ehe, Naunyn Schmiedebergs Arch Pharmacol, 280 (1973) 265.
[3] F. Villalpando-Vargas, L. Medina-Ceja, Seizure, 39 (2016) 49.
[4] D. Scharnagel, J. Goller, N. Deibl, W. Milius, M. Breuning, Angew Chem, 57 (2018) 2456
[5] N. Maulide, B. Peng, C. A. M. Afonso, R. F. M. Frade, WO2014/191261, 2014.

Acknowledgments

We thank the FCT for financial support (UIDB/04138/2020, UIDP/04138/2020, UIDB/00100/2020, UIDP/00100/2020 and LA/P/0056/2020) and PTDC/QUI-QOR/1786/2021. The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996. JASC thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND.

POSTER COMMUNICATION

HYPERBARIC STORAGE AS A CELL PRESERVATION METHODOLOGY – CAN BLOOD BE STORED UNDER PRESSURE?

Ana P. Martins[1,2], Álvaro T. Lemos[1], Tiago R. Correia[2], Brian J. Goodfellow[2], João F. Mano[2], Jorge A. Saraiva[1*]

[1] LAQV-REQUIMTE, Chemistry Department, Aveiro University, Portugal; [2] CICECO, Chemistry Department, Aveiro University, Portugal; *jorgesaraiva@ua.pt

In some low/middle-income countries, blood preservation for transfusion remains a challenge [1]. Therefore, it is essential to develop new techniques that can improve blood preservation or storage in more difficult circumstances. Hyperbaric storage (HS) is a new preservation methodology that allows the storage of products under pressure (up to 100 MPa) for variable time periods and has been studied almost exclusively in food products [2]. When used at uncontrolled room temperature, this methodology is a quasi-energetically costless procedure since, after pressure generation, no additional energy is required to keep it along storage, allowing energetic savings [3]. So, hyperbaric storage has been studied as a potential new blood preservation methodology. Whole swine blood, with CPDA-1, was stored for 35 days under pressure (25 – 75 MPa) at variable uncontrolled room temperature and refrigeration temperatures and compared to a conventional whole blood preservation method (refrigeration). To study whole blood during storage, quantification of hemolysis, pH measurement, and a multivariate and metabolic composition analysis (NMR) were performed.

The results demonstrate that pressures above 50 MPa, regardless of temperature, promote cell lysis. However, at lower pressures (25 – 45 MPa) and variable uncontrolled room temperature, it was possible to maintain hemolysis values below 0.8 % up to 12 days with minimal energy consumption. At the same pressures but combined with refrigeration temperatures (5 °C) better hemolysis results were obtained with values below the limit during 35 days of storage. However, when compared to the conventional method (refrigeration), the values were approximately the same. The metabolic composition analysis revealed a lower lactate and a higher glucose concentration in blood stored under pressure, which may indicate a decrease in red blood cell metabolic rates when pressure and refrigeration temperatures are combined.

This study gives a global perspective on the viability of using hyperbaric storage as a whole blood preservation technique. To have a deeper insight, additional research and analysis are required, such as flow cytometry for microvesicles detection and microscopy for morphology characterization.

References

[1] M., Del, M. García-Roa, C. Vicente-Ayuso, A. M. Bobes, A. C. Pedraza, A. González-Fernández, M. P. Martín, I. Sáez, J. Seghatchian, L. Gutiérrez, Blood Transfusion, 15(2017) 222–253.

[2] Á. T. Lemos, A. C. Ribeiro, L. G. Fidalgo, I. Delgadillo, J. A. Saraiva, Food Chemistry, 231 (2017) 61–69.

[3] A. Bermejo-Prada, A. Colmant, L. Otero, B. Guignon, Journal of Food Engineering, 193 (2017) 76–85.

Acknowledgments

Thanks are due to University of Aveiro and FCT/MCT for the financial support to LAQV-REQUIMTE research Unit (UIDB/50006/2020 & UIDP/50006/2020) through national founds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement. This work was also 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/MEC (PIDDAC). Ana P. Martins also acknowledges FCT/MCT for the PhD grant reference SFRH/BD/146369/2019 and Álvaro T. Lemos for the PhD grant reference SFRH/BD/129848/2017

ANALYSIS OF DIFFERENT METHODS TO CALCULATE PERMEABILITY COEFFICIENTS

Margarida M. Cordeiro,[1*] Armindo Salvador,[1,2,3] Maria João Moreno[1,2]

[1]Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS), Universidade de Coimbra, Portugal; [2]Centro de Neurociências e Biologia Celular, Universidade de Coimbra, Portugal; [3]Instituto de Investigação Interdisciplinar, Universidade de Coimbra, Portugal. *mmc.margarida0@gmail.com

Unassisted permeation through biomembranes is of outmost importance for the availability of drugs and biological ligands at their target site. The pH variation assay is one of the few methodologies appropriated to characterise the permeation of non-fluorescent weak acids/bases. Permeability coefficients are obtained by following the dynamics of a pH fluorescent probe. Current protocols of this assay only focus on the study of the fast generation of the pH gradient and have raised several concerns which are preventing its generalised use. To transform this assay into a reliable tool, we developed a detailed kinetic model that allowed us to identify the experimental conditions needed to warrant an accurate characterisation of the dynamics of the weak acid/base permeation from the fluorescence variation and evaluate different methods to obtain their permeability coefficient (Figure 1).[1] The results showed that the often-used expression $P_{app}^{r} = \beta\, r/3$ is inapplicable to very large or very small vesicles, to moderately or highly lipophilic solutes, or when the development of a significant pH gradient opposes the solute's flux. We anticipate that the resolution of all these concerns and the study of the fast generation and slow dissipation of the pH gradient can turn the pH variation into an important tool to analyse and better understand the general rules of unassisted permeation through biomembranes.

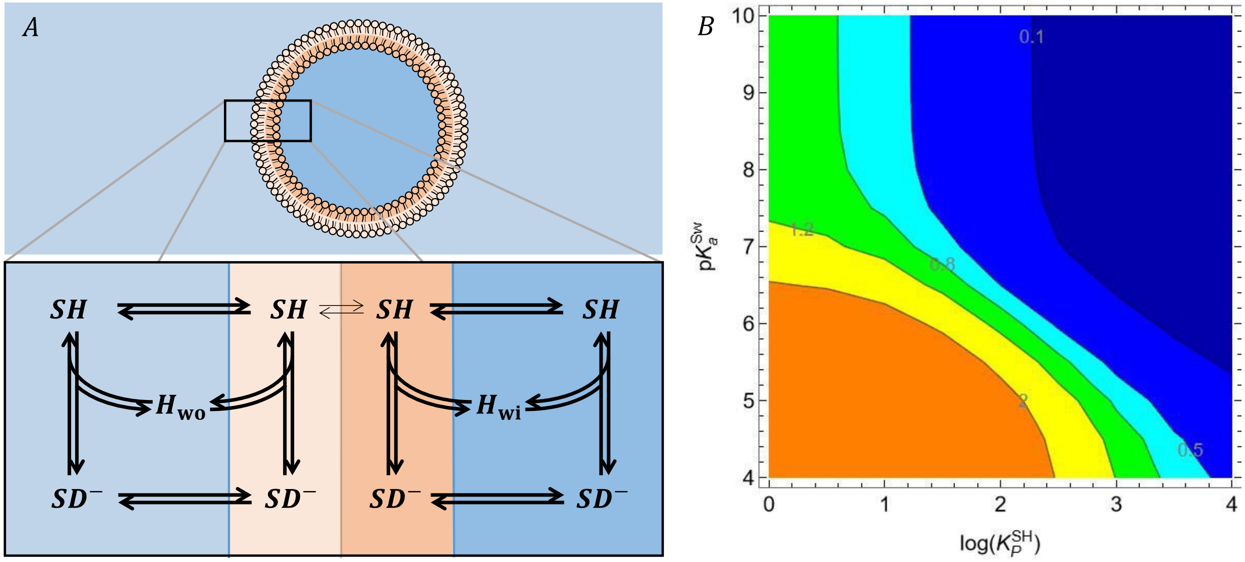


Figure 1: **A)** Kinetic scheme for the permeation of a weak acid through lipid membranes. **B)** Validity domains of the simplified procedure usually followed to calculate permeability coefficients from solute dynamics.

References

[1] Cordeiro, M. M., Salvador, A. & Moreno, M. J. Membranes. 12, (2022) 254.

Acknowledgments

Work financed by COMPETE 2020, under projects UIDB/00313/2020, UIDP/00313/2020 and UIDB/04539/2020

P3

NEW TROJAN HORSES DESIGNED TO OVERCOME ANTIFUNGAL RESISTANCE

Joana Cardoso,[1,2,3,*] Eugénia Pinto, [2,3] Emília Sousa,[1,3] Diana Resende, [1,3]

[1]Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy of the University of Porto, 4050-313 Porto, Portugal; [2]Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy of the University of Porto, 4050-313 Porto, Portugal; [3]Interdisciplinary Centre of Marine and Environmental Research (CIIMAR), University of Porto, 4450-208 Matosinhos, Portugal.
*dresende@ff.up.pt

Fungal infections are one of the leading causes of mortality and morbidity worldwide, especially in immunocompromised patients. This fact, allied with the relatively increasing incidence of resistant strains to the few classic antifungal drugs provided by their indiscriminate use, makes it necessary to discover and develop new therapeutic strategies [1]. One hypothesis to overcome this resistance is by manipulating microbial iron transport pathways to deliver antimicrobials to the cell using siderophores, often called the "Trojan horse" approach [2]. Particularly, siderophore-antibiotic conjugates have already demonstrated such promise in therapeutics [3] while the conjugation of siderophores with antifungal drugs is practically unexplored. This conjugation of iron-chelating microbial siderophores to antifungal agents could also be hypothesized to enhance uptake, intracellular concentration and antifungal efficacy, and subsequently control the emergence of new resistances [4].

Based on these considerations, the present work explores the design, synthesis, and lead generation of siderophores mimetics to explore the potential of these compounds conjugated with in-house and/or commercial antifungals. The first strategy towards the synthesis of this small library of conjugates involved the synthesis of 2,3-bis(benzyloxy)benzoic acid, a molecule frequently found in naturally occurring siderophores and which served as a structural backbone to obtain the desired siderophore mimetics. The compounds were achieved through an amide coupling between 2,3-bis(benzyloxy)benzoic acid and commercially available primary amines as building blocks facilitated by several coupling reagents (CDI, DCC, and COMU). The structure elucidation of all the synthesized compounds was established by nuclear magnetic resonance (NMR) spectroscopy. Complexation properties with different metals of all synthesized compounds and their antifungal activity will be explored in the future.

References

[1] C. Joana, F-S. Joana, D. Fernado, C. Diogo, G. Luís, P. Madalena, S. Emília, P. Eugénia, Antibiotics, 11 (2022) 1488.
[2] B. Meenakshi, C. Renu, R. Sonam, S. Bharat, D. Nisha, S.P. Virinder, P.K, Jaiwal, K.C. Anil, Expert Opinion on Therapeutic Targets, 20 (2016) 1477-1489.
[3] K. Behnoush, M. Pezhman, M. Abdolmajid, Microbiological Research, 250 (2021), 126790.
[4] P. Joachim, B. Roland, H. Isabella, H.A. Anton, G. Fabio, H. Hubertus Haas, D. Clemens, Journal of Fungi, 6 (2020), 367.

Acknowledgements

This research was supported by national funds through FCT - Foundation for Science and Technology within the scope of UIDB/04423/2020, UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry, CIIMAR), projects EXPL/CTA-AMB/0810/2021, and by the Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement and through the ERDF, as a result of the project ATLANTIDA (reference NORTE-01-0145-FEDER-000040). Joana Cardoso acknowledges FCT for the individual PhD grant (2022.10043.BD) and Diana I. S. P. Resende for her individual researcher contract (2022.00379.CEECIND).

P4

SYNTHESIS OF SIDEROPHORE MIMETICS AND CONJUGATION WITH ANTIBACTERIAL ADJUVANTS FOR MEDICINAL AND ENVIRONMENTAL APPLICATIONS

Mariana C. Almeida,[1,2] Paulo M. da Costa,[2,3] Emília Sousa,[1,2] Diana I. S. P. Resende [1,2*]

[1]Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge de 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]ICBAS – Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal.
*dresende@ff.up.pt

Siderophores are metal chelating compounds with a high affinity for iron, which are produced by a variety of organisms, such as bacteria, fungi and some plants.[1] Both naturally-occurring siderophores and synthetic mimetics have shown potential in diverse fields, such as drug development, diagnostic, bioremediation and food industry.[2] One interesting approach consists in the conjugation of siderophores with antimicrobial agents as a way of circumventing drug resistance.[3] Inspired by the enormous potential of siderophore-conjugated molecules, in this work we aim to conjugate natural siderophores or synthetic mimetics with known antibacterial adjuvants to obtain new dual agents with medicinal and environmental applications.

To achieve this goal, first, several siderophore mimetics were synthesized. Then, a known antibacterial adjuvant was coupled with different linker portions and the obtained molecules were finally coupled with the siderophore mimetics to yield the siderophore-antibacterial conjugate. Structural elucidation of all synthesized compounds was achieved by nuclear magnetic resonance (NMR) techniques. Current work includes the expansion of the library of siderophore-antibacterial conjugates and, in the near future, the evaluation of their antibacterial potential against a panel of human and fish pathogenic bacteria as well as the assessment of mechanisms related to bacteria virulence.

References

[1] Ahmed, E.; Holmström, S. J. M., Microbial Biotechnology, 7 (2014) 196-208.
[2] De Serrano, L. O., Biomolecular Concepts, 8 (2017) 169-178.
[3] Almeida, M. C.; da Costa, P. M.; Sousa, E.; Resende, D. I. S. P., Journal of Medicinal Chemistry, 66 (2023) 32-70.

Acknowledgments

This research was supported by national funds through FCT - Foundation for Science and Technology within the scope of UIDB/04423/2020, UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry, CIIMAR) and project EXPL/CTA-AMB/0810/2021, under the PORTUGAL 2020 Partnership Agreement. Mariana C. Almeida acknowledges FCT for the individual PhD grant (2021.05224.BD) and Diana I. S. P. Resende for her individual researcher contract (2022.00379.CEECIND).

P5

NEW CHIRAL 6,7-BIS(HYDROXYMETHYL)-1H,3H-PYRROLO[1,2-C]THIAZOLES AS P-53 ACTIVATING AGENTS FOR COLORECTAL CANCER TARGETED THERAPY

Ana Beatriz Pereira[1]*, Carla Carvalho[2], Maria I. L. Soares[1], Lucília Saraiva[2], Teresa M. V. D. Pinho e Melo[1]

[1]University of Coimbra, Coimbra Chemistry Centre (CQC) – Institute of Molecular Sciences and Department of Chemistry, 3004-535 Coimbra, Portugal

[2]LAQV/REQUIMTE, Laboratório de Microbiologia, Departamento de Ciências Biológicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal

**anaspereira_2000@hotmail.com*

Colorectal cancer (CRC) is the third most common cancer type and the second cause of cancer-related deaths worldwide.[1] Advances in understanding the pathogenesis of CRC demonstrated that disfunctions in p53 protein are a critical event in local and advanced CRCs. Therefore, re-establishing p53 activity has become one of the most appealing anticancer therapeutic strategies to treat CRC. Recently, the group found a new p53-activating anticancer drug, (3*S*)-6,7-bis(hydroxymethyl)-5-methyl-3-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole (MANIO).[2] MANIO is a selective p53 activator, which activates both wild-type p53 and several mutated forms with high clinical prevalence The aim of this study focused on the structural modulation of the lead compound, MANIO, in order to obtain MANIO-like derivatives with optimized pharmacokinetic and pharmacodynamic properties. The synthetic strategies explore several structural changes around the 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole scaffold (Fig.1), namely the introduction of alkyl groups in C-1 (e.g. **1**), replacement of the phenyl group by other aryl or heteroaryl groups (e.g. **2**) and the oxidation to sulfoxides or sulfones (e.g. **3**). In this communication, these approaches will be presented as well as some preliminary results on biological activity of the new derivatives as anticancer agents.

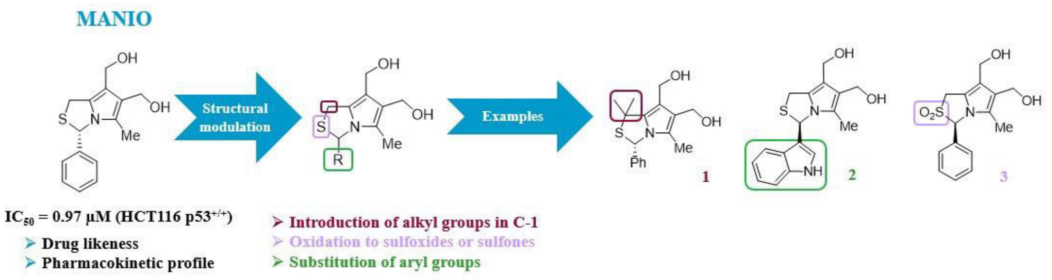


Figure 1. Structural modulation of MANIO.

References

[1] H. Sung, J. Ferlay, R. L. Siegel, M. Laversanne, I. Soerjomataram, A. Jemal, F. Bray *CA Cancer J. Clin*. **2021**, *71*, 209-249.
[2] H. Ramos, M. I. L. Soares, J. Silva, L. Raimundo, J. Calheiros, C. Gomes, F. Reis, F. A. Monteiro, C. Nunes, S. Reis, B. Bosco, S. Piazza, L. Domingues, P. Chlapek, P. Vlcek, P. Fabian, A. T. Rajado, A. T. P. Carvalho, R. Veselska, A. Inga, T. M. V. D. Pinho E Melo, L. Saraiva *Cell Rep.* **2021**, *35*, 108982.

Acknowledgements: This work was supported by PT National Funds (FCT/MCTES, Fundação para a Ciência e Tecnologia, and Ministério da Ciência, Tecnologia e Ensino Superior) via the projects UIDB/00313/2020 (CQC), UIDP/00313/2020 (CQC) and UIDB/50006/2020 (LAQV/REQUIMTE), co-funded by COMPETE2020-UE. J.L.P.R. thanks FCT for the PhD fellowship PD/BD/143160/2019 (MedChemTrain programme)". The authors also acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt).

P6

EXPLORING THE PYRROLO[1,2-*C*]THIAZOLE SCAFFOLD: DESIGN OF NOVEL P53-ACTIVACTING AGENTS FOR COLORECTAL CANCER THERAPY

Adelino M. R. Pereira,[1*] Carla Carvalho,[2] Maria I. L. Soares,[1] Lucília Saraiva,[2] Teresa M. V. D. Pinho e Melo[1]

[1]University of Coimbra, Coimbra Chemistry Centre (CQC) – Institute of Molecular Sciences and Department of Chemistry, 3004-535 Coimbra, Portugal; [2]LAQV/REQUINTE and Department of Biological Sciences, University of Porto, 4050-313 Porto, Portugal. *adelinomrp1@gmail.com

Colorectal cancer (CRC) is the third most common cancer type and one of the leading causes of cancer-related deaths worldwide [1], and its treatment lacks effectiveness. Recent advances in understanding the pathogenesis of CRC demonstrated that impairment of the p53 pathway, especially dysfunctions of the p53 protein, is a critical event in this type of cancer. Thus, p53 is a very appealing molecular target to treat CRC. Recently, we disclosed a new p53-activating molecule with potential to become an anticancer drug, (3*S*)-6,7-bis(hydroxymethyl)-5-methyl-3-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole (MANIO, **Figure 1a**) [2]. MANIO demonstrated a notable selectivity to the p53 pathway, not only activating wild-type (WT)p53 but also restoring the function of mutant (mut)p53 in human cancer cells. Further research in patient-derived cells and xenograft mouse models of CRC, confirmed the high efficacy of MANIO and showed no signs of undesirable side effects. Therefore, MANIO is a lead compound with great potential to become an anticancer drug. In this communication, lead optimization studies aiming at developing MANIO-like derivatives with improved pharmacodynamics and pharmacokinetics properties will be presented (**Figure 1b**).

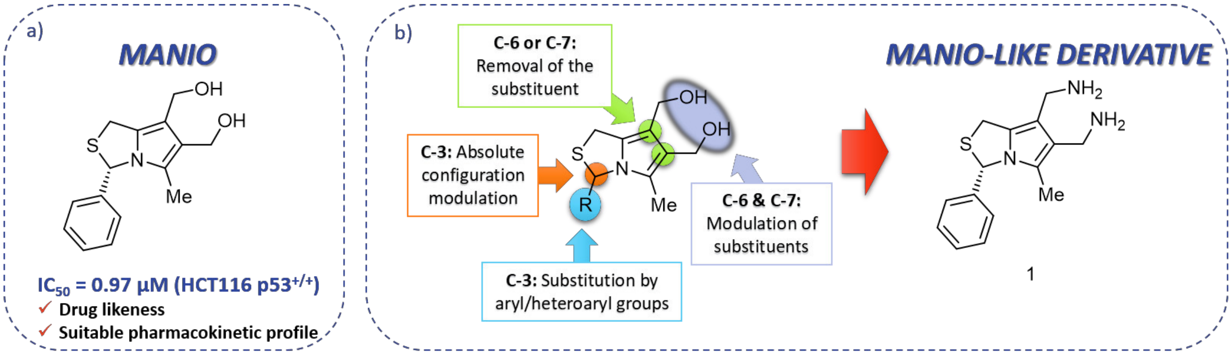


Figure 1: a) MANIO; b) Structural modulation of MANIO.

References

[1] H. Sung, J. Ferlay, R. L. Siegel, M. Laversanne, I. Soerjomataram, A. Jemal, F. Bray, CA Cancer J. Clin, 71 (2021) 209-249.
[2] H. Ramos, M. I. L. Soares, J. Silva, L. Raimundo, J. Calheiros, C. Gomes, F. Reis, F. A. Monteiro, C. Nunes, S. Reis, B. Bosco, S. Piazza, L. Domingues, P. Chlapek, P. Vlcek, P. Fabian, A. T. Rajado, A. T. P. Carvalho, R. Veselska, A. Inga, T. M. V. D. Pinho e Melo, L. Saraiva, Cell Rep, 35 (2021), 108982.

Acknowledgments

This work was supported by PT National Funds (FCT/MCTES, Fundação para a Ciência e Tecnologia, and Ministério da Ciência, Tecnologia e Ensino Superior) via the projects UIDB/00313/2020 (CQC), UIDP/00313/2020 (CQC) and UIDB/50006/2020 (LAQV/REQUINTE), co-funded by COMPETE2020-UE. The authors also acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt).

P7

BODIPY DYES FOR PHOTODYNAMIC THERAPY OF CANCER

Chrislaura Carmo[1]*, Juliana Araújo[1], Maria Filomena Botelho[2,3,4], Mafalda Laranjo[2,3,4], Armando Cordova[5], Abílio J. F. N. Sobral[1]

[1]Chemistry Department, FCTUC, University of Coimbra, 3004-535, Coimbra, Portugal, [2]Institute of Biophysics and Institute for Clinical and Biomedical Research (iCBR), [3]Center for Innovative Biomedicine and Biotechnology (CIBB), [4]Clinical and Academic Centre of Coimbra, 3000-548 Coimbra, Portugal. [5]Faculty of Science, Technology and Media, Department of Natural Sciences, Mid Sweden University, Sweden. *cribego@gmail.com

Photodynamic therapy (PDT) is currently used as an alternative treatment for many malignant and non-malignant diseases. In PDT, a photosensitizing agent absorbs light of a particular wavelength and produces singlet oxygen (^{1}O2) and other reactive oxygen species, resulting in cell death [1]. PDT is minimally invasive with selective action on tumor tissue making it a particularly interesting therapeutic approach for oncologic diseases [2]. This work aimed to synthesize, characterize, and evaluate the metabolic activity of a new class of emerging BODIPY PDT agents. BODIPY 1(2,8-diethyl-5,5-difluoro-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-*f*] [1,3,2] diazaborinin-4-ium-5-uide) was synthesized from the 3-ethyl-2,4-dimethyl-1H-pyrrole and 4-hydroxybenzaldehyde, in CH_2Cl_2 followed by *in situ* oxidation with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), and complexation with $BF_3 \cdot OEt_2$ in the presence of the base[3]. BODIPY 2 (10-(4-(allyloxy) phenyl)-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-dipyrrolo[1,2-c:2',1'-*f*] [1,3,2] diazaborinin-4-ium-5-uide) was synthesized from BODIPY 1 and allyl bromide, in acetonitrile, in presence of potassium carbonate, figure 1. The BODIPYs were characterized by standard analytical and electrochemical techniques, including UV-Vis spectroscopy, ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR, and mass spectrometry.

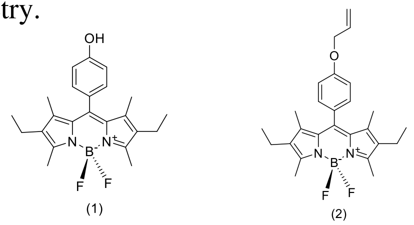


Figure 1: Molecular structure BODIPYs 1 and 2

BODIPYs at concentrations between 100 μM -1μM were added in breast cancer cell lines (MCF-7 and HCC-1806) for 24 hours. Cancer cells were irradiated with green light (532nm) and red light (640 nm) with 10 J. The cytotoxicity (MTT) assessment was performed for BODIPYs after 24 hours of PDT. IC_{50} (half maximal inhibitory concentration) from BODIPYs 1 and 2 are represented in table 1.

Table 1: IC_{50} - MTT of BODIPYs 1 and 2 in two breast cancer cells lines

	MCF-7			HCC-1806		
	IC_{50} green light	IC_{50} red light	IC_{50} without irradiation	IC_{50} green light	IC_{50} red light	IC_{50} without irradiation
BODIPY 1	1.71	9.56	29.86	0.87	3.71	38,68
BODIPY 2	2.94	16.47	31.59	1.48	3.31	IC_{50} > Max

References

[1] José H. Correia, José A. Rodrigues, Sara Pimenta, Pharmaceutics, 2021, 13, 1332.
[2] Mafalda Laranjo, Márcia Campos Aguiar, European Journal of Medicinal Chemistry, 200 (2020) 112468.
[3] Mengdi Liu, Siyue Ma, Mengyao She, Chinese Chemical Letters, 30 (2019) 1815–1824.

Acknowledgments

The authors thank the Coimbra Chemistry Centre (CQC), the Institute of Biophysics, and the Institute for Clinical and Biomedical Research (iCBR).

P8

CORRELATING ZEOLITE CHARACTERISTICS WITH SYNTHESIS CONDITIONS: FROM COMPREHENSIVE DATASETS TO MACHINE LEARNING MODELS

Maria Leonor Frazão,[1] Daniel P. Costa,[1] Pedro S. F. Mendes[1*]

[1]Departamento de Engenharia Química & Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

Due to their specific characteristics, Zeolites, a type of aluminosilicate crystals, present a wide range of applications, being catalysis one of them. Correlating their properties with the preparation conditions through models would speed up the optimization of these materials, avoiding excessive time spent in trial- and-error optimization [1]. However, the physical processes behind the zeolite preparation are very complex which difficult the creation of such models. A blackbox input-output model could solve this problem. This project ultimately aims to correlate zeolite synthesis conditions with the produced characteristics via Machine Learning models [2]. To do so, a comprehensive zeolite database is also aimed to be created.

Based on a database search, it was found that, despite the great amount of information gathered and studied over the years, the lack of a single database containing all necessary information complicates the proposed process. A complex artificial dataset will then be created, having per base simpler ones, where the machine learning models will be applied. This multidimensional dataset has multiple inputs and outputs, being their relationship highly nonlinear, necessitating the use of machine learning models to extract meaningful correlations between synthesis conditions and zeolite properties.

Among the many Machine Learning approaches researched, using supervised learning was found to be the best way to tackle this challenge. Artificial Neural Networks (ANN), Random Forest Regression (RFR), and Support Vector Regression (SVR) are seemingly the most adapted methods that should be explored given the nonlinearity and multiple outputs of the data. The methods will be assessed having into consideration evaluation metrics, such as accuracy, precision and recall or cross-validation.

In conclusion, the lack of a comprehensive database and the complexity of the data were identified as the key challenges to apply machine learning models to this specific problem. Nevertheless, within supervised machine learning, suitable ML methods that can be well-adjusted to the complexity and particularities of the datasets were selected, making it possible to extract meaningful information. In this way, we will employ an artificial dataset to understand if the ML-based methodology is viable to be later applied to an experimental dataset, and which are the most promising supervised methods and models to be utilized.

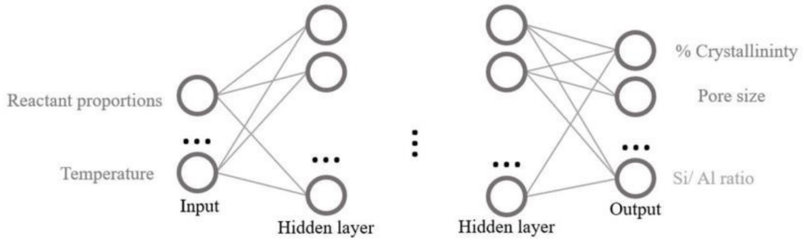


Figure 1: Simplified representation of the ANN model to be utilized in this project, showing relevant input and output parameters

References

[1] X. Zhang, D. Tang, M. Zhang and R. Yang, Powder Technology, 235, 322-328, 2013.
[2] Z. Jensen, E. Kim, S. Kwon, T. Gani, Y. Román-Leshkov, M. Molioner, A. Corma and E. Olivetti, ACS central science, 5, 892-899, 2019

Acknowledgments

The authors acknowledge the FCT funding to CQE (UIDB/00100/2020 e UIDP/00100/2020) and EU H2020 funding via EOSC Future to Pedro Mendes' ambassadorship (101017536).

P9

ESTIMATION OF DROPLETS DIAMETER IN A LIQUID-LIQUID EXTRACTION COLUMN USING IMAGE PROCESSING METHODS

Helena Vendas,[1] Remígio Machado,[1] Catarina Barata,[2] Pedro S. F. Mendes[1*]

[1]Departamento de Engenharia Química, [2]Instituto de Sistemas e Robótica, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal; *pedro.f.mendes@tecnico.ulisboa.pt

There is a significant interest in automating processes to enhance efficiency, accuracy and reliability in data acquisition. This study uses image processing techniques to automate the estimation of droplets' diameter in liquid-liquid extraction (LLE) columns. This approach has practical implications, as it can contribute to the identification of the optimal operating conditions for LLE processes, resulting in more efficient mass transfer between liquids.

The goal of this study is to develop an efficient and reliable method that uses image processing techniques to estimate the diameter of droplets in a LLE column (see Figure 1). To achieve this, cameras are placed along the column height to capture high quality images. The effectiveness of object detection relies heavily on selecting suitable image pre-processing techniques, including treatments and filters like blurring for noise reduction, contrast enhancement, and edge sharpening to ensure that the objects are distinguishable from the background.

After pre-processing the images, mathematical methods are applied to estimate the droplets diameter. These methods primarily rely on processing grayscale images to detect object boundaries by identifying pixel value gradients. Grayscale images simplify the processing task as they only require a single matrix to represent the image, with each element corresponding to a gray value.

Due to the simplicity in implementation, mathematical models were selected for edge identification and object segmentation rather than machine learning models, which would have required significantly more images and time for training, testing, and validation. The chosen approach is based on the definition of a circle, which involves identifying multiple points that belong to the same boundary and are equidistant from a central point. This approach is effective for detecting circles in images and is widely used in various research areas, given the simplicity and good results of this method [1][2]. To utilize this method effectively, it was necessary to optimize several parameters to improve the accuracy of identified circles in an image and increase the overall number of circles detected.

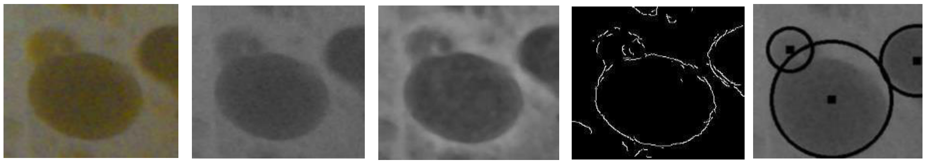

(a) (b) (c) (d) (e)

Figure 1: Visual representation of the several processes applied to the images: (a) Original; (b) Grayscale; (c) Application of the pretreatment for the noise reduction, contrast and sharpening enhancement; (d) Edge detection; (e) Circle identification

In conclusion, by applying these methods to a large number of images, from different parts of the column, a big number of droplets can be accurately identified, and their diameter recorded. Having this data recorded can later be used to develop a machine learning model that simulates the column behavior.

References
[1] Meng, Y., Zhang, Z., Yin, H., & Ma, T. (2018). Micron, 106, 34 41. doi:10.1016/j.micron.2017.12.002
[2] Yamaguchi, T., & Mizutani, T. (2021). Automation in Construction, 126, 103651. doi:10.1016/j.autcon.2021.10365

Acknowledgments
The authors acknowledge Instituto Superior Técnico for the funding via the Pedagogical Innovation Project 1018P.06228.

P10

NEW ANTIDOTES FOR *BOTHROPS ASPER* VENOM: STUDY OF PLA2 PROTEIN

Roberto Pinto,[1] Ana Rita Calixto,[2] Maria João Ramos,[2] Pedro G. Ferreira[3,4], Pedro Fernandes[2]

[1]Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto; [2]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto; [3]Department of Computer Science, Faculty of Sciences of the University of Porto, Porto, Portugal; [4]Laboratory of Artificial Intelligence and Decision Support, Institute for Systems and Computer Engineering, Technology and Science, Porto, Portugal

Nowadays, it's estimated that 1.8 to 2.7 million people develop clinical illnesses, and 81-138 thousand die from venom from snakebite complications. So, it's urgent to find a therapy that acts quickly and effectively. Snake venoms are complex mixtures of small molecules, peptides, and proteins, that display significant bioactivity, like neurotoxicity, cytotoxicity, and cardiotoxicity. The venom composition differs from snake to snake, but there are 4 proteins that are the most common: snake venom metalloproteinase (SVMP), snake venom serine protease (SVSP), secreted phospholipase A2 (PLA2), and the 3-finger toxins (3FTxs). Secreted phospholipase A2 are multi-toxic enzymes that can cause both local and systemic effects, having mostly a myotoxic effect. The most notable targets of PLA2 are skeletal muscle fibers, the neuromuscular junction, and the hemostatic system. These types of enzymes require the presence of calcium (Ca^{2+}) for their activity. The project focuses on understanding the reaction mechanism of PLA2 of *Bothrops asper* using a chromogenic substrate, NOBA, and obtaining compounds that can inhibit this enzyme.

Molecular docking was the first methodology to be applied to predict the ideal pose of NOBA. For that, GOLD was used to perform 50 runs with a radius of 10 Å, using four different scoring functions of Gold. After this, a 4-step minimization of the complex was applied, using an octahedral box of water molecules with 15 Å beyond the protein extremities. Molecular dynamics simulations were also made with an NPT ensemble at 310.15 K. Then, molecular docking was validated: the results were compared with several structures of PLA2 that have a substrate, ligand, or inhibitor, using the four scoring functions of GOLD. GoldScore was the scoring function that had better results. Several MD simulations were made to see the stability of the protein, especially the residues that coordinate the calcium. Using the protocol of frozen atoms or distance restraints, releasing the restraints causes modifications in the coordination, especially the interaction NOBA-Calcium. With those results, it's possible to see that the coordination is very labile. Future work involves further molecular dynamics simulation, a QM/MM study on the enzyme, and applying machine learning in the drug discovery process.

MOLECULAR DESCRIPTORS FOR THE CHARACTERIZATION OF ANTIBIOTICS: COMBINING MACHINE LEARNING AND AB INITIO CALCULATIONS

Dário Cartaxo, Francisco Fonseca, Ana Patrício, Sandra Nunes, Tânia F. Cova*, Alberto A. C. C. Pais

Coimbra Chemistry Centre, Department of Chemistry, Institute of Molecular Sciences (IMS), Faculty of Sciences and Technology,
University of Coimbra, 3004-535 Coimbra, Portugal
*tfirmino.gc@qui.uc.pt

Bacterial resistance is a serious public health problem, which led the World Health Organization (WHO) to recognize the relevance of studies that address this issue. Modelling the behaviour of priority antibacterial molecules for the WHO using molecular descriptors aims to contribute to the creation of new tools and methodologies that allow for the rapid and efficient characterization of antibacterial molecules based on their chemical profile and the most relevant antibiotic families for the WHO.[1] Specifically, a set of antibiotic molecules referenced by the WHO as presenting concerning levels of bacterial resistance were characterized, using electronic structure calculations and machine learning methods to characterize and correlate the structural and molecular characteristics and the known families of these compounds with their biological activity. The combination of two unsupervised computational learning methods, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA)[2, 3], allowed for the determination of the most relevant molecular descriptors for discriminating between antibiotic families and for forming groups with common structural characteristics. The identified groups are consistent with known antibiotic families, suggesting that molecules belonging to the same group have similar structural and molecular characteristics. Additionally, Principal Component Analysis allowed for establishing the relationship between the distribution of molecules in the defined groups and the molecular descriptors. The results showed that the molecular descriptors with the greatest impact for discriminating antibacterial molecules are nAtomLac, MDEN.33, FMF, VC.6, VCH.3, VCH.7, C1SP2, C3SP2, ATSc3, ATSc5, and apol. In conclusion, the unsupervised analysis implemented in this study allowed for the rapid and efficient characterization of different antibiotic families that are responsible for the growth of bacterial resistance. The results obtained allow for the establishment of a classification methodology for antibacterial molecules without the need for experimental studies.

References

[1] C. S.Vinagreiro, A. Zangirolami, F. A. Schaberle, S. C. C. Nunes, K. C. Blanco, N. M. Inada, G. J. da Silva, A. Pais, V. S. Bagnato, L. G. Arnaut, M. M. Pereira, ACS Infect. Dis., 2020, 6 (2020) 1517-1526.
[2] J. Basso, M. Mendes, J. Silva, T. Cova, E. Luque-Michel, A. F. Jorge, S. Grijalvo, L. Gonçalves, R. Eritja, M. J. Blanco-Prieto, A. J. Almeida, A. Pais, C. Vitorino, International Journal of Pharmaceutics, 592 (2021) 120095.
[3] T. Cova, A. A. C. C. Pais, Frontiers in Chemistry 7 (2019).

Acknowledgments

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), the Portuguese Agency for Scientific Research for the financial support through projects UIDP/00313/2020. Tânia Cova acknowledge the Junior Researcher Grant CEECIND/00915/2018 assigned by FCT.

P12

CHARACTERIZING EMERGING PSYCHOACTIVE DRUGS BY MINING CHEMICAL DATA AND USING MOLECULAR SIMULATIONS

Tânia F. Cova*, Sandra Nunes, Soraia Assis, Alberto A. C. C. Pais

Coimbra Chemistry Centre, Department of Chemistry, Institute of Molecular Sciences (IMS), Faculty of Sciences and Technology, University of Coimbra, 3004-535 Coimbra, Portugal.
*tfirmino@qui.uc.pt

New Psychoactive Substances (NPS) have emerged as a significant public health concern, and it is widely believed that the knowledge about these substances is only the tip of an iceberg. Due to the exponential increase in the number of NPS, the pharmacological effects of these substances are poorly understood. This work aims to develop a methodology that can quickly and efficiently characterize unknown NPS based on the chemical profile of regulated NPS. To achieve this goal, a combination of two unsupervised analysis methods, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), were used.[1, 2] PCA identified the molecular descriptors that are most relevant to the discrimination of NPS families, and HCA enabled the identification of groups of NPS with common characteristics. Validation of the clusters obtained through this methodology was done using molecular dynamics (MD) simulations and docking. Specifically, three NPS molecules from the Synthetic Cannabinoids family, CS12_C, CS33_C, and CS55_NI, were selected for further characterization using MD and Docking.

The results obtained from the chemometrics analysis showed the formation of three distinct groups based on the molecular descriptors, and six groups based on common characteristics. The results from MD and docking showed that the behaviour of a single molecule in a model membrane did not allow for clear discrimination between the NPS, but the inclusion of other components in the membrane could provide better results. Docking results revealed common patterns and characteristics between CS33_C and CS55_NI, but not for CS12_C. Although it is not possible to make a clear distinction, it is noticeable that the behaviour of molecules CS33_C and CS55_NI is practically identical, and small differences can be observed when compared to the results of molecule CS12_C. Therefore, we believe that the behavior of NSPs may be more discriminative if conditions change, such as the addition of other components to the model biomembrane or the addition of more molecules to the system. Additionally, docking studies were conducted to evaluate the interaction between these molecules and the Cannabinoid Receptor 1 (CB1). With this method, the similarities between the CS33_C and CS55_NI pair and the differences with molecule CS12_C were explicit. However, it would be interesting to evaluate this interaction through MD method because, unlike docking, DM grants the receptor-NSP system flexibility instead of a rigid system.

The proposed methodology can contribute to the development of a better understanding of the pharmacological effects of NPS, which can ultimately inform public health policies and interventions.

References

[1] T. Cova, A. Pais. Frontiers in Chemistry 7 (2019).
[2] J. Basso, M. Mendes, J. Silva, T. Cova, E. Luque-Michel, A. F. Jorge, et al. International Journal of Pharmaceutics 592 (2021) 120095.

Acknowledgments

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), the Portuguese Agency for Scientific Research for the financial support through projects UIDP/00313/2020. Tânia Cova acknowledge the Junior Researcher Grant CEECIND/00915/2018 assigned by FCT.

DNA NANOSTRUCTURES AS ANTIMICROBIAL DRUG NANOCARRIERS: A MOLECULAR DYNAMICS STUDY

Sandra C.C. Nunes*,[1] Tânia Cova,[1] Ana Luísa C. Ferreira[1], A.A.C.C. Pais[1]

[1]Coimbra Chemistry Center, Chemistry Department of the University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal.
*snunes@qui.uc.pt

Antimicrobial resistance is currently a major public health concern and a scientific challenge. Due to the rapid growth of infectious diseases, the increase in bacterial resistance and the slow development of new antibiotics with new mechanisms of action, different approaches have been proposed to combat this problem, including the design of new molecules or new delivery systems [1]. Cytotoxicity or lack of stability have prevented the effective application of these materials [2-4]. In this context, we consider that DNA-based nanotechnology [5,6] is a promising tool to develop alternatives for the delivery of antimicrobial agents to fight the problem of antimicrobial resistance.

In this work, a systematic Molecular Dynamics study is proposed to explore the behavior and the patterns of interaction between a DNA origami structure with triangular shape and a model drug, the ciprofloxacin, an antibiotic used to treat a significant number of bacterial infections especially those caused by Gram-Negative bacteria. The results obtained from Molecular Dynamics simulations show that the origami DNA structure used is stable in all tested conditions and that its interaction with the model drug molecule increases the structural stability. It was possible to identify and quantify the main molecular interactions responsible for the stability of the complex. This type of computational models are versatile allowing to characterize and optimize different complex systems of biomedical interest [7,8]. These results support the potential of these DNA-based structures as antimicrobial nanocarriers.

References

[1] C. S. Vinagreiro, A. Zangirolami, F. A. Schaberle, S. C.C. Nunes, K. C. Blanco, N. M. Inada, G. J. da Silva, A. C. C. Pais, V. S. Bagnato, L. G. Arnaut, M. Pereira, ACS Infect. Dis. (2020) 6, 6, 1517–1526.
[2] Lázár, V., et al., Nature Microbiology, 2018. 3(6): p. 718-731.
[3] Panáček, A., et al., Nature Nanotechnology, 2018. 13(1): p. 65-71.
[4] Luther, A., et al., Nature, 2019. 576(7787): p. 452-458.
[5] Xie, N., et al., Analyst, 2017. 142(18): p. 3322-3332.
[6] Wang, J., et al., ACS Central Science, 2019. 5(5): p. 755-767.
[7] A. C. Solís, D. Bento, S. C.C. Nunes, A. Valente, A. Pais, C. Vitorino, Polymer 230 (2021) 124032
[8] M. Mendes, S.C.C. Nunes, J. J. Sousa, A. A. C. C. Pais, C. Vitorino, Molecular Pharmaceutics (2017) 14 (6), 2099–2115.

Acknowledgments

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), the Portuguese Agency for Scientific Research for the financial support through projects UIDP/00313/2020. Tania Cova acknowledge the Junior Researcher Grant CEECIND/00915/2018 assigned by FCT.

IN SILICO DEVELOPMENT OF NOVEL POLYMYXIN B DERIVATIVES: QSAR MODELS OF ANTIMICROBIAL ACTIVITY

João Miguel Inácio[1,2,3], Paula Jorge[2,3], Filipe Teixeira[1*]

[1] Centre of Chemistry, University of Minho, 4710-057 Braga, Portugal; [2]Centre of Biological Engineering, University of Minho, 4710-057 Braga, Portugal; [3]LABBELS – Associate Laboratory, Braga/Guimarães, Portugal.
*fteixeira@quimica.uminho.pt

Multidrug-resistant (MDR) microorganisms are a major health threat, as they can transform everyday small infections into life-threatening situations. MDR infections not only pose an immediate life risk, but also increased morbidity and healthcare and social security costs [1]. Polymyxin B is a clinically approved "last resort" drug to fight MDR infections due to its high effectiveness but unfortunate toxicity; however, resistance to this peptide has already been reported [2]. Thus, computational tools allowing the design of new molecules with promising antimicrobial activity towards MDR strains are of great interest. This work aimed at developing predictive models of antimicrobial activity of polymyxin-derived structures, starting from the collected antimicrobial activity (evaluated as the Minimum Inhibitory Concentration, MIC) of 610 molecules/microorganism combinations. Four classification models were developed, namely logistic regression, decision trees, random forest, and AdaBoost, with different families of molecular descriptors (**Figure 1**). The AdaBoost classification model with Hall and Keir connectivity indexes [3] as descriptors proved to be the best, with an accuracy of 74% and with only 2.3% probability of classifying a low-active compound as very active. This model has already been applied and predicted promising activity for 6 different polymyxin analogs that are currently being synthesised and will be soon tested for their antimicrobial and toxicological profiles.

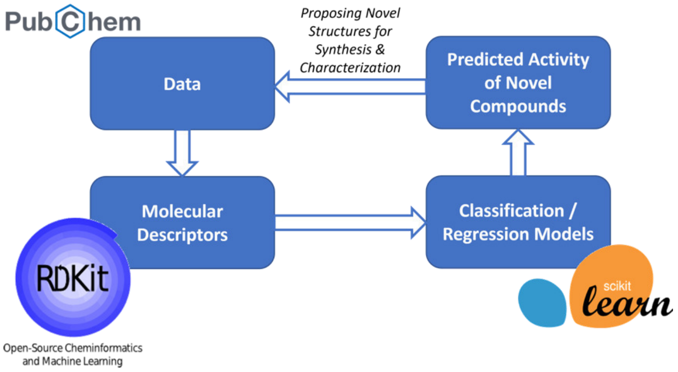


Figure 1. Flowchart of the *in silico* development of novel antimicrobial compounds.

References

[1] Jorge P, Magalhães AP, Grainha T, Alves D, Sousa AM, Lopes SP, Pereira MO. Antimicrobial resistance three ways: healthcare crisis, major concepts and the relevance of biofilms. FEMS Microbiol Ecol. 95 (2019) fiz115.
[2] Nang SC, Azad MAK, Velkov T, Zhou QT, Li J. Rescuing the Last-Line Polymyxins: Achievements and Challenges. Pharmacol Rev. 73 (2021) 679.
[3] Hall LH, Kier LB. The Molecular Connectivity Chi Indexes and Kappa Shape Indexes in Structure-Property Modeling. Reviews in Computational Chemistry. 2 (2007) 367.

Acknowledgments

This work was supported by the Portuguese Foundation for Science and Technology (FCT) under the scope of project POLYmix-POLYmic (2022.06595.PTDC), of the programmatic funding to CQUM (UID/QUI/00686/2020), of the strategic funding to CEB (UIDB/04469/2020), of the contract CEECIND/00194/2020, and by LABBELS - Associate Laboratory in Biotechnology, Bioengineering and Microelectromechanical Systems (LA/P/0029/2020).

GREENHOUSE GASES SOLUBILITY BY MAGNETIC IONIC LIQUIDS: MD SIMULATION STUDY

Andreia P. Fonseca*, Nádia M. Figueiredo, Iuliia V. Voroshylova, M. Natália D. S. Cordeiro

LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
*up201703595@fc.up.pt

Recently, the increase of greenhouse gases (such as CO_2 and CH_4) emission has become one of the major environmental concerns. In this context, the capture and separation of polluting gases becomes a necessity for various environmental causes. Moreover, the captured gases can be further reused for other purposes, for example, they can be applied in the synthesis of other organic compounds [1].

Ionic liquids (ILs), a class of organic salts with low melting points (less than 100 °C) and low vapor pressures, have been studied for gas separation since the beginning of the 2000s, although the first record on ILs dates back to 1914 [2]. One of ILs' attractive feature is the possibility to synthesize them with different combinations of cations and anions, thus controlling their selectivity and solubility towards different gases [3]. Magnetic ionic liquids (MILs) have turned to be common choice for gas capture since they respond to external magnetic field due to incorporated paramagnetic atoms [4]; they can also be highly hydrophobic and present large magnetic susceptibility [5]. Metal chloride anions generally have excellent NH_3 or CO_2 adsorption capacity, as these molecules contain unshared electron pairs and consequently can act as ligands.

Upon the development of green chemistry, it is crucial to use methods which allow to avoid waste of reactants. For that reason, molecular dynamics (MD) simulations become a good option, since they permit collecting valuable information on studied systems in an ecofriendly manner.

In this work, we performed MD simulations using GROMACS 2020.4 software package. We focus on the adsorption of CO_2 in MILs based on trihexyl(tetradecyl)phosphonium cation, [P_{66614}], coupled with chlorometallate (Fe(III), Mn(II) and Gd(III)) anions. [P_{66614}][$FeCl_4$] was also explored for the possibility of other potentially dangerous gases capture. The results were rationalized in terms of free energy of solvation, radial and spatial distribution functions. The effect of the temperature on the gas capture process was also addressed.

References
[1] Feider, N.O., et al., *Molecular dynamics simulations of a dicationic ionic liquid for CO2 capture.* Journal of Molecular Liquids, 2021. **335**: p. 116163.
[2] Singh, S.K. and A.W. Savoy, *Ionic liquids synthesis and applications: An overview.* Journal of Molecular Liquids, 2020. **297**: p. 112038.
[3] Lei, Z., C. Dai, and B. Chen, *Gas solubility in ionic liquids.* Chemical reviews, 2014. **114**(2): p. 1289-1326.
[4] Santos, E., et al., *Synthesis and characterization of magnetic ionic liquids (MILs) for CO2 separation.* Journal of Chemical Technology & Biotechnology, 2014. **89**(6): p. 866-871.
[5] Pierson, S.A., et al., *Synthesis and characterization of low viscosity hexafluoroacetylacetonate-based hydrophobic magnetic ionic liquids.* New Journal of Chemistry, 2017. **41**(13): p. 5498-5505.

Acknowledgments
This work was supported by UIDB/50006/2020 with funding from FCT/MCTES through national funds. N.M.F. further acknowledges the ChemMat Ph.D. programme and FCT for the grant PD/BD/150419/2019.

TOXIC DINOFLAGELLATES (*DINOPHYSIS* SPP.) DETECTION BY GENOSENSORS AND MOLECULAR BIOLOGY APPROACHES

Eduarda Pereira[1,2], Aurora Silva[2,3], Stephanie L. Morais[2], Estefanía Costa-Rama[2], Patrícia R. Moreira[4], M. Fraga-Corral[3], Ana M. Torrado[3], Francisco Rodríguez[5,6], Piedade Barros[1], Agostinho Cruz[1], Cristina Delerue-Matos[2], M.A. Prieto[3], J. Simal-Gandara[3], Nádia F. D. Silva[2], Marlene Santos[1,7], M. Fátima Barroso[2]*

[1]CISA|ESS, Centro de Investigação em Saúde e Ambiente, Escola Superior de Saúde, Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 400, 4200-072, Porto, Portugal; [2]REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072, 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]Universidade Católica Portuguesa, CITAR - Centro de Investigação em Ciência e Tecnologia das Artes, Escola das Artes, Rua Diogo Botelho 1327, 4169-005, Porto, Portugal; [5]Centro Nacional Instituto Español de Oceanografía (IEO-CSIC), Centro Oceanográfico de Vigo, 36390 Vigo, Spain; [6]Europen Reference Laboratory for Monitoring of Marine Biotoxins (EURLMB), Citexvi, University of Vigo, 36310 Vigo, Spain; [7]Molecular Oncology & Viral Pathology, IPO- Porto Research Center (CI-IPOP), Portuguese Institute of Oncology, Porto, Portugal. *mfb@isep.ipp.pt

Over the years, the marine ecosystems integrity has been compromised, due to multiple factors that disrupt the natural balance of phytoplankton. Factors such as the unregulated runoff of agricultural and industrial wastes into the aquatic environment and higher surface temperatures [1] are believed to have transformed these ecosystems into favorable habitats for algae growth and proliferation. As a result, multiple species may produce harmful toxins that significantly affect the integrity of rivers, lakes, estuaries, and coastal areas [2]. Although these microorganisms are mostly harmless, certain species, namely belonging to dinoflagellates (e.g. *Dinophysis* spp.) produce toxins that pose a risk for human health. Therefore, the need for technological developments towards fast and precise detection of these toxin-producing microalgae is critical to prevent socioeconomical damages, as well as to assess the ecological status of marine ecosystems. The goal of this work was to develop analytical approaches based on electrochemical genosensors devices in order to create a low-cost platform able to detect two dinoflagellate species from the genus *Dinophysis*: *D. acuminata* and *D. acuta*, which are lipophilic toxin producers responsible for diarrhetic shellfish poisoning (DSP) in humans [3]. The design of this DNA-based sensor consists of three steps: i) Sensing phase: consisted by a mixed self-assembled monolayer composed by a linear DNA capture probe and mercaptohexanol onto disposable screen-printed gold electrodes surface; ii) Hybridization of complementary DNA sequence (DNA target) by using a sandwich format assay with enzymatic labels and iii) Electrochemical detection by chronoamperometry using an enzymatic scheme to amplify the electrochemical signal. The best analytical conditions used to study the relationship between electrochemical signal and DNA target concentration, to produce the best electrochemical genosensor device are described in Table 1. Molecular biology tools were used to validate the electrochemical genosensor.

Table 1: Optimized analytical variables in the development of the electrochemical genosensor.

Variables evaluated	Tested range	Selected value
DNA-capture probe concentration (µM)	0.25-1.00	0.25
MCH concentration (µM)	0.00-1.00	0.10
MCH incubation time (min)	15-60	7.5
Homogeneous hybridization incubation time (min)	15-60	30
Antibody concentration (µM)	0.5-2	2
Antibody incubation time (min)	15-60	60
Heterogeneous hybridization incubation time (min)	15-60	60
Homogeneous hybridization temperature (ºC)	25, 98	98

References

[1] Development of harmful algal blooms species responsible for lipophilic and amnesic shellfish poisoning intoxications in southwestern Mediterranean coastal waters. Aboualaalaa, H. et al., Toxicon, 2019 (2022); [2] Electrochemical genosensor for the detection of Alexandrium minutum dinoflagellates. Morais, S. L. et al., Talanta 222 (2021); [3] Marine Biotoxins: Occurrence, Toxicity, Regulatory Limits and Reference Methods. Visciano, P. et al., Front. Microbiol. 7 (2016) 1051.

Acknowledgments

Authors are grateful to Ibero-American Program on Science and Technology (CYTED — GENOPSYSEN, P222RT0117) and to the financial support from the European Union and National Funds (FCT, Fundação para a Ciência e Tecnologia) through projects UID/QUI/50006/2019. MFB (2020.03107.CEECIND) is grateful to Fundação para a Ciência e a Tecnologia (FCT) and European Union (EU) for the grant, financed by POPH-QREN-Tipologia 4.1-Formação Avançada, funded by Fundo Social Europeu (FSE) and Ministério da Ciência, Tecnologia e Ensino Superior (MCTES).

DEVELOPMENT AND CHARACTERIZATION OF SOLID LIPID NANOPARTICLES FORMULATIONS IN NUTRIENTS DELIVERY FOR ANIMAL FEED

Daniela Oliveira,[1] Beatriz Silva,[1] Paula Gomes,[2] Sofia A. Costa Lima,[3] Salette Reis[1*]

[1]Department of Chemical Sciences, LAQV, REQUIMTE – Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal; [2]Chemistry Department, LAQV, REQUIMTE – Faculty of Sciences, University of Porto, Rua do Campo Alegre, 687 s/n, 4169-007, Porto, Portugal; [3]Chemistry Department, LAQV - REQUIMTE, ICBAS – School of Medicine and Biomedical Sciences, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal.
*shreis@ff.up.pt

Along with the human population growth, the animal production sector and the number of domestic animals has significantly increased. Consequently, the development of fortified pet food and feed with greater functional interest has become a subject of high importance. Nowadays, animal food are fortified through the incorporation of important nutrients, such as, vitamins, fats, and peptides. However, some of these nutrients are mainly degraded during the manufacturing and storage processes, decreasing the quality of the feed [1].

In this context, the encapsulation of nutrients with functional interest in nanoparticles emerges as a solution to overcome the problem aforementioned. Thus, this work aimed to develop and characterize solid lipid nanoparticles (SLNs) containing vitamin K3 and a functional peptide (PpT2 [2]), which are easily degraded during the production of the animal feed, to assure their protection and stability.

SLNs were prepared using the hot homogenization method. Firstly, different compositions and concentrations of lipids and surfactants were tested to choose the best vehicles for the vitamin and the peptide. More than 80 % and 99 % of the vitamin K3 and the PpT2, respectively, were entrapped in the produced nanoparticles. Furthermore, the particle size, polydispersity and peptide content in the SLNs were, so far, stable after 1 month of storage at the room temperature. The two potential formulations obtained, containing or not vitamin K3 and PpT2, were subjected to *in vitro* assays simulating gastrointestinal digestion and demonstrated to be stable in the stomach. Also, SLNs showed no toxicity in fibroblasts (L929) for concentrations lower than 2 mg mL^{-1} (PpT2-free SLNs) and 1.5 mg mL^{-1} (PpT2-loaded SLNs). Therefore, the two formulations developed proved to have potential to continue to be investigated and likely to be integrated as nanocarriers in animal feed fortification or added in the animal diet as supplements.

References

[1] Q. D. Tran, W. H. Hendriks, A. F. & van der Poel, Journal of the Science of Food and Agriculture, 88 (2008) 1487-1493.
[2] A. Plácido et al., Journal of Cellular and Molecular Medicine, 26 (2022) 2793-2807.

Acknowledgments/Funding

Financial support of NovInDog - Novos Ingredientes Proteicos Funcionais para a Alimentação de Cães: uma Abordagem Sustentável (POCI-01-0247-FEDER-047003) funded by national funds and co-financed by European Regional Development Fund (ERDF) to the research and to DO are acknowledge. SCL is thankful to Fundação para a Ciência e a Tecnologia (FCT) for the Researcher grant (FCT/MEC [CEECINST/00007/2021).

P18

OBTENTION AND CHARACTERIZATION OF A POLYPHENOL ENRICHED EXTRACT FROM OLIVE POMACE

Gabriel Azevedo,[1] Sofia Lima,[2] Salette Reis,[1*]

[1]LAQV, REQUIMTE, FFUP, Rua de Jorge Viterbo Ferreira, 228 4050-313 Porto, Portugal; [2]LAQV - REQUIMTE, ICBAS – School of Medicine and Biomedical Sciences, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313, Porto, Portugal.
*shreis@ff.up.pt

Polyphenols are a chemically diverse class of compounds that have antioxidant activity and thus can prevent systemic and/or localised inflammation by restoring the redox balance and via modulating inflammatory responses [1]. These biochemical characteristics of polyphenols are associated with a decrease in risks of several diseases making them compounds of interest [2, 3]. These are mainly obtained through the diet since they can be found in a variety of foods, like fruits and vegetables [4]. However, processed food based on antioxidant rich fruits and vegetables do not always conserve these in the final product.

One such example is olive oil. Its industry by-products, like olive pomace (OP) and olive oil wastewater, conserve higher amounts of phenolic compounds compared to the olive oil produced due to their chemical characteristics. Having this in mind, a simple extraction design was accessed to recover these compounds and any remaining lipids. For this, olive pomace was kindly given by a local olive oil mill in Mirandela, Portugal, collected after the pressing stage. Fresh pomace was lyophilized, to reduce the water content, and extracted through an ultrasound-assisted extraction in different conditions and using a couple of eco-friendly solvents in order to optimise the extraction of polyphenols and any remaining lipids. The extracts were then characterised regarding its antioxidant activity, through multiple assays, as well as polyphenol and lipid content. The optimized extract showed an activity of 3,49 ± 0,22 mg GAE/ g OP in the Folin-Ciocalteu assay as well as 1,69 ± 0,04 mg TEA/ g OP in the DPPH antioxidant assay.

This work seeks to confer an added value to the olive oil industry through its by-product and to promote a circular economy concept *via* the execution of a simple, fast, and eco-friendly extraction to recover its retained polyphenols and residual lipids.

References
[1] Zhang, H.; Tsao, R., Dietary polyphenols, oxidative stress and antioxidant and anti-inflammatory effects. Current Opinion in Food Science 2016 33-42.
[2] Fraga, C. G.; Croft, K. D.; Kennedy, D. O.; Tomas-Barberan, F. A., The effects of polyphenols and other bioactives on human health. Food Funct 2019 514-528.
[3] Cory, H.; Passarelli, S.; Szeto, J.; Tamez, M.; Mattei, J., The Role of Polyphenols in Human Health and Food Systems: A Mini-Review. Front Nutr 2018 87.
[4] Manach, C.; Scalbert, A.; Morand, C.; Remesy, C.; Jimenez, L., Polyphenols: food sources and bioavailability. Am J Clin Nutr 2004 727-47.

Acknowledgments
Financial support of “NovInDog - Novos Ingredientes Proteicos Funcionais para a Alimentação de Cães: uma Abordagem Sustentável” (POCI-01-0247-FEDER-047003) funded by national funds and co-financed by European Regional Development Fund (ERDF) to the research and to GA are acknowledge. SCL is thankful to Fundação para a Ciência e a Tecnologia (FCT) for the Researcher grant (FCT/MEC [CEECINST/00007/2021).

P19

IMPACT OF AMMONIACAL NITROGEN ON THE CENTESIMAL COMPOSITION AND CHEMICAL PROFILE OF *PORTULACA OLERACEA* L.

Paschoalinotto, B. H.[1,2,3], Chrysargyris, A.[4]; Aiex, V. A. P.[1,2]; Petropoulos, S.[5]; Tzortzakis, N.[4]; Prieto, M.A.[3]; 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; **maria.ines@ipb.pt*

[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]Cyprus University of Technology, Department of Agricultural Sciences, Biotechnology and Food Science, Anexartisias 33, 3036, Limassol, Cyprus;

[5]Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 38446 Volos, Greece.

Purslane (*Portulaca oleracea* L.) is a wild edible plant that is highly appreciated for its therapeutic properties. Its leaves and stems are commonly consumed as juices, as well as raw or cooked in salads. Recently, purslane has been classified as a functional food due to its high nutritional value, which has generated great interest in its production through commercial cultivation [1-2]. It is a species highly adaptable to various adverse conditions, which makes it a promising species for cultivation under environmental stressors. Nitrogen fertilization plays an important role in the development of primary and secondary plant metabolites. Moreover, several studies indicate that the form of the nitrogen source can affect the final content and the profile of the compounds produced [1,3]. Therefore, the objective of this study was to evaluate the effect of different percentages of ammoniacal nitrogen in fertilization on the centesimal and chemical profiles of *Portulaca oleracea* leaves and stems using AOAC and chromatographic methods. The results showed that purslane leaves contained higher amounts of total fat and protein, while stems contained higher amounts of total dietary fiber and carbohydrates. Oxalic, succinic, and fumaric acids were also identified in all the samples, whereas only the α-tocopherol isoform was present in purslane tissues. Stems contained fructose, glucose, sucrose, and trehalose, whereas leaves contained only fructose and glucose. Linoleic acid was mostly found in the stems, while linolenic acid was more prevalent in the leaves. Based on this preliminary study, it was observed that the amount of ammoniacal nitrogen had an impact on valuable macronutrients, namely crude protein, and total dietary fiber suggesting that tailor made nutrient solution may increase the quality and the nutritional value of the edible product.

References

[1] E. Fontana, J. Hoeberechts, S. Nicola, V. Cros, G. B. Palmegiano, and P. G. Peiretti, *J Sci Food Agric*, 86 (2006) 2417–2424.
[2] S. Petropoulos, A. Karkanis, N. Martins, and I. C. F. R. Ferreira, *Trends Food Sci Technol*, 55 (2016) 1-10.
[3] Y. Zhang, X. Lin, Y. Zhang, J. Z. Shao, and S. Du, *Journal of Plant Nutrition*, 28 (2007) 2011–2025.

Acknowledgments

To the Foundation for Science and Technology (FCT, Portugal) for the financial support through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); to FCT for the financial support to the VALUEFARM project (PRIMA/0009/2019) - PRIMA Section 2 - Multitopic 2019; to FCT national funds, P.I., under the institutional scientific employment contract of L. Barros and M.I. Dias. To MICINN for the Ramón y Cajal fellowship of M.A. Prieto (RYC-2017-22891); to the General Secretariat for Research and Technology (GSRT) of Greece and PRIMA Foundation for the Valuefarm project (Prima 2019-11) with co-funding by the Funding Agencies RIF – Cyprus.

NATURAL COATING FORMULATIONS TO PRESERVE CHESTNUTS

Felipe Alves[1,2], Liege A. Pascoalino[1,2], Márcio Carocho[1,2], Alexandre Gonçalves[3], Luana Fernandes[3], Jorge Moreira[4], Filipe Lema[1,2], Elsa Ramalhosa[1,2], 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]MORE– Laboratório Colaborativo Montanhas de Investigação – Associação, Edifício do Brigantia Ecopark, Avª Cidade de Leon, 506, 5300-358 Bragança Bragança, Portugal; [4]Sortegel - Produtos Congelados, S.A., Rua S. Mamede Nr. 25, 5300-903 Sortes, Bragança. *sheleno@ipb.pt

Chestnuts are highly appreciated and widely consumed throughout Europe, America, and Asia [1]. They represent a strong economic value, especially in the Trás-os-Montes region (Portugal), which contributes with 84% of the total Portuguese production [3]. However, there is a great loss of the product during storage due to weight loss and microbial degradation [4]. Therefore, there is a need to create techniques that guarantee the extension of the chestnut, maintaining its quality.

The study aimed to evaluate the impacts of different natural coatings, such as wax, chitosan, chitosan+rosemary, chitosan+wax, and chitosan+wax+rosemary, as well as a commercial coating, on chestnuts. The analysis of individual fatty acids was performed by GC-FID and the antioxidant activity was measured by the ability to inhibit the formation of thiobarbituric acid reactive substances (TBARs assay) for three different storage times: 0 (T0), 7 (T1), and 21 (T3) days. It was also investigated the effect of various coatings on the external and internal color and texture of chestnuts during storage, using a Minolta CR-400 colorimeter by applying the CIELab scale and a TA-XTPlus Texture Analyser, respectively. At T0, the wax coating showed the highest content of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids, 1.61± 0.06 and 1.75 ± 0.01 g/100g dw, respectively, compared to the levels obtained by the commercial coating at 1.39 ± 0.06 and 1.59 ± 0.02 g/100g dw, respectively. At T1 and T3, the chitosan+wax coating was more effective than the commercial one, showing 1.70 ± 0.005 g/100g dw and 0.65 ± 0.03 g/100g and 1.19 ± 0.01 and 1.94 ± 0.02 g/100g dw, respectively. The chitosan+rosemary coating exhibited the best antioxidant activity at both T0 and T1, providing protection against oxidation and revealing the strongest EC_{50} values (0.71 ± 0.01 mg/mL and 0.35 ± 0.03 mg/mL, respectively); however, the EC_{50} value increased to 1.48 mg/mL at T3 for the same coating.

All coatings increased the luminosity of chestnuts after 7 and 21 days, and no significant changes in texture or internal color were observed. The wax coating had the most consistent behavior in terms of water activity and moisture content.

In conclusion, all chitosan-based coatings were more effective after seven days. However, further approaches are needed to determine the most suitable coating to act as an efficient preserving agent, by analysing other chestnut characteristics, such as the organoleptic ones.

References

[1] Calandrelli, M. M., Nunziata, A., & De Masi, L. (2023). Pilot Study on the Geographical Mapping of Genetic Diversity among European Chestnut (*Castanea sativa* Mill.) Cultivars in Southern Italy. Plants, 12(4), 917. https://doi.org/10.3390/plants12040917

[2] Borges, O., Gonçalves, B., de Carvalho, J. L. S., Correia, P., & Silva, A. P. (2008). Nutritional quality of chestnut (*Castanea sativa* Mill.) cultivars from Portugal. Food Chemistry, 106(3), 976–984. https://doi.org/10.1016/j.foodchem.2007.07.011

[3] Uzun, S. (2023). Postharvest Quality Traits of Chestnut (*Castanea sativa* Mill.) Fruit as Affected by Methyl Jasmonate During Cold Storage. Erwerbs-Obstbau. https://doi.org/10.1007/s10341-023-00851-6.

Acknowledgments

FCT through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); S. Heleno thanks FCT for her individual employment program–contract (CEECIND/03040/2017), and L. Barros also thanks to the national funding by FCT through the institutional scientific employment program–contract for her contract; and for Liege A. Pascoalino PhD grant. To the European Regional Development Fund (ERDF) for financial support to the project RevestCast (POCI-01-0247- FEDER-04927.

P21

SELENIUM BIOFORTIFICATION OF PLANTS AND MUSHROOMS: TOWARDS HEALTHIER FOODS FOR HUMAN NUTRITION – AN OVERVIEW

Roberto A. Costa,[1,2,3] Alexis Pereira,[1,2,4] Carla Pereira,[1,2] José Pinela,[1,2] Pablo A. Garcia,[3] Lillian Barros,[1,2] Maria Inês Dias[1,2*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal. *maria.ines@ipb.pt
[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]Department of Pharmaceutical Sciences, Pharmaceutical Chemistry Section, Faculty of Pharmacy, IBSAL, University of Salamanca, Salamanca, 37007, Spain.
[4]Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E-32004 Ourense, Spain.

Today, many people suffer from micronutrient deficiencies due to the lack of nutrient-dense foods in their daily diet. Selenium is an essential trace element for human nutrition as it is a key component of several enzymes and proteins with critical biological functions [1]. Its deficiency affects up to one billion people worldwide and has been linked with serious human diseases, such as certain types of cancer and cardiovascular problems [2,3]. Although selenium is not an essential element for plants, food crops grown in selenium-poor soils inevitably have low levels of this element. Furthermore, since moderate climate change projections (2080–2099) indicate 8.7% soil selenium losses in 66% of croplands [4], the worldwide prevalence of selenium deficiency could be exacerbated. Therefore, crop biofortification emerges as a sustainable approach to provide selenium-enriched foods to an increasing world population. This study aimed to highlight the most promising inorganic forms of selenium for biofortification of mushrooms from Montesinho Natural Park and baby leaf Swiss chard based on available literature [5,6]. Selenium has been supplied to plants and mushrooms most often in the anionic forms of selenite (SeO32−) and selenate (SeO42−) via foliar and soil application in the case of plants or by addition to the mushroom growing substrate. In general, selenate has been reported to be more effective for biofortification of plant crops due to its faster uptake and translocation and subsequent transformation into organic forms as compared to selenite. However, the effectiveness can be influenced by nutrient fertilization, presence of microorganisms, and plant variety, among other factors. On the other hand, the selenium bioaccessibility seems to be higher from sodium selenite-enriched mushrooms. This salt promotes mushroom growth when added at low concentrations, while an opposite result is obtained at high concentrations. Biofortification is also a strategy to improve the bioactivity of food crops, as inorganic selenium is transformed into organic metabolites such as selenium-polysaccharides, selenoproteins, and selenoamino acids. Still, a better understanding of the effects of selenium on the growth and metabolism of plant and mushroom species is important to obtain high quality and healthy foods.

References

[1] W.B. Minich, Biochemistry (Mosc). 87 (2022) S168.
[2] A.O. Rataan, S.M. Geary, Y. Zakharia, et al., International Journal of Molecular Sciences, 23 (2022) 2215.
[3] B.K. Shimada, N. Alfulaij, L.A. Seale, International Journal of Molecular Sciences, 22 (2021) 10713.
[4] G.D. Jones, B. Droz, P. Greve, et al., Proceedings of the National Academy of Sciences, 114 (2017) 2848.
[5] M. Xu, S. Zhu, Y. Li, et al., Trends in Food Science & Technology, 118 (2021) 328.
[6] G. Izydorczyk, B. Ligas, K. Mikula, et al., Science of the Total Environment, 754 (2021) 141983.

Acknowledgments

The authors thank the Foundation for Science and Technology (FCT, Portugal) for the financial support through national fun FCT/MCTES to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2021); to FCT for the contracts C. Pereira (CEEC Institutional), J. Pinela (CEECIND/01011/2018), L. Barros (CEEC Institutional) and M.I. Dias (CEEC Institutional) and for the project MTS/BRB/0056/2020 (Safe2Taste).

P22

VEGETABLES LOSSES AND WASTES AS A SOURCE OF BIOBASED INGREDIENTS

Joana P. B. Rodrigues,[1,2] Ângela Liberal,[1,2] Spyridon A. Petropoulos,[3] Isabel C. F. R. Ferreira,[1,2] Maria Beatriz P. P. Oliveira,[4] Ângela Fernandes,[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]Laboratory of Vegetable Prouction, Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, Fytokou Street, N. Ionia, 384 46 Volos, Greece; [4]REQUIMTE/Department of Chemical Sciences, Faculty os Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira no. 228, 4050-313 Porto, Portugal. *afeitor@ipb.pt

The constant growth of world's population and consumers' concern to sustain a healthy diet put a challenge to the agricultural sector which has to ensure a sustainable food supply and food safety at the same time. In recent years, the growing consumption of fruit and vegetables has increased their production and consequently the volume of agri-food surplus, waste, and loss (SWL) generated during their production, transportation, storage, and processing [1]. According to FAO, about 42% of fruit and vegetables that are produced worldwide are lost or wasted even before reaching the consumer, while a large part is discarded in landfills representing a major threat to the environment and reducing the added value of the corresponding crops [2]. The valorization of agri-food SWL through their recovery and reuse is a challenge. Usually, these by-products are valuable sources of compounds of interest, such as, proteins, fibers, phenolic compounds, vitamins, among others, and are associated with beneficial effects on human health and well-being. Lettuce, carrots and broccoli are among the most consumed vegetables worldwide, due to their nutritional and chemical particularities, thus resulting in the production of large amounts of waste throughout the food supply chain [3,4,5]. Thus, in this work we explored the efficient management of agri-food SWL of these particular vegetables, considering conventional and emerging recovery and reuse techniques, and we summarized the nutritional and chemical composition of raw products and their waste, aiming to valorize their SWLs as important sources of bio-based ingredients, with potential uses in the formulation of a wide variety of new biodynamic formulations.

References

[1] F. Dilucia, V Lacivita, A. Conte, M. Del Nobile, Foods, 9 (2020) 857.
[2] FAO. Global Food Losses and FoodWaste–Extent, Causes and Prevention. SAVE FOOD: An Initiative on Food Loss and Waste Reduction. Available online: https://www.fao.org/3/i2697e/i2697e.pdf
[3] T. Nasrin, A. Matin, in Food Processing By-Products and their Utilization, A. Anal, Wiley: Hoboken, NJ, USA, 2017; pp. 53–88.
[4] G. Kaur, V. Orsat, A. Singh, British Food Journal, 123 (2021) 2036-2048.
[5] P. Bachiega, J. Salgado, J. Carvalho, A. Ruiz, K. Schwarz, T. Tezotto, M. Morzelle, Food Chemistry, 190 (2016) 771-77

P23

Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national FCT/MCTES to CIMO (UIDB/00690/2020) and SusTEC (LA/P/0007/2021). National funding by FCT, P.I., throug institutional scientific employment program-contract for L. Barros and A. Fernandes contracts, and J. Rodrigues PhD fello p (UIBD/153744/2022).

EVALUATION OF PHENOLIC EXTRACTION METHOD ON THE ANTIOXIDANT CAPACITY OF RED GRAPES AT DIFFERENT MATURATION STAGES

Tatiane Otto de França,[1] Cláudia M.B. Neves,[2] Renato V. Botelho,[1] Luiz A. Biasi,[3] Ana C. Correia,[2] António M. Jordão[2,4*]

[1] Universidade Estadual do Centro-Oeste do Paraná, Departamento de Ciências Agrárias, Guarapuava, Paraná, Brasil; [2] Instituto Politécnico de Viseu, Escola Superior Agrária, Viseu, Portugal; [3] Universidade Federal do Paraná, Departamento de Ciências Agrárias, Curitiba, Paraná, Brasil; [4] Centro de Química de Vila Real, Portugal; *antoniojordao@esav.ipv.pt

Grapes are one of the most important fruit commodities, as economic plants, with good agricultural characteristics being also an important source of antioxidants, such as polyphenols. These compounds confer several benefits to human health, performing biochemical and pharmacological effects such as anticancer, anti-inflammatory, antimicrobial, and antioxidant activities [1]. The composition and content of grape phenolic compounds and consequently their antioxidant or antiradical capacity could be affected by many factors, such as grape variety, climate conditions, and ripening stage [2]. Extraction is the first step of polyphenolic analysis, which consists in isolation of phenolic compounds from plant materials. So, the used method in this procedure becomes essential for the accurate quantification and determination of antioxidant capacity. Several extraction conditions are reported in the literature, however there is no single extraction method which may be considered standard.

Thus, the main objective of this work was to evaluate the effect of the extraction method on the antioxidant capacity of red grapes from *Touriga Nacional* variety at different stages of maturation and from different vine locations. For this, the determination of the antioxidant capacity was carried out from phenolic extracts obtained by the application of the Carbonneau and Champagnol method [3], which is one of the most used methodologies for phenolic extraction from grapes. The results obtained were compared with the evaluation of the antioxidant activity carried out directly on the grape musts. For the antioxidant capacity quantification two methods were used: $ABTS^{\bullet+}$ scavenging activity [4] and $DPPH^{\bullet}$ scavenging activity [5]. In addition, total phenolic content was evaluated using the method described by Ribéreau-Gayon et al. [6]. The results obtained showed that the concentration of total phenolics in the extracts obtained by the Carbonneau and Champagnol method was higher than the values obtained directly in grape musts. For example, at technological maturity, for phenolic extracts, the total phenolic content varied between 0.73 and 1.36 mg/g of berry, while for grape musts the values varied between 0.27 and 0.60 mg/g of berry. A similar behavior was found for the antioxidant capacity, where the extracts showed higher antioxidant capacity when compared with the results obtained directly from the grape musts. Thus, at technical maturity, the antioxidant activity of the extracts ranged from 4.49 to 11.14 mmol/L Trolox for $DPPH^{\bullet}$, while using $ABTS^{\bullet+}$ scavenging method, the values ranged from 8.27 to 13.43 mmol/L Trolox. A different tendency was observed for grape musts where lower antioxidant capacity was quantified (values ranging from 0.66 to 4.35 mmol/L Trolox for $DPPH^{\bullet}$ and from 1.43 to 3.22 mmol/L Trolox for $ABTS^{\bullet+}$). The results obtained in this work show the importance of the phenolic extraction methodology for a correct determination of antioxidant capacity in grapes.

References

[1] Darra et al., Food and Nutrition Sciences, 3 (2012) 1420-1432.
[2] Cosme et al., European Food Research and Technology, 241 (2015) 61-73.
[3] Carbonneau and Champagnol, Programme AIR-3-CT93 (1993).
[4] Re et al., Free Radical Biology & Medicine, 26 (1999) 1231-1237.
[5] Brand-Williams et al., Food Science and Technology, 28 (1995) 25-30.
[6] Ribéreau-Gayon et al., Science et Techniques du vin, 1982 Tome 4.

P24

Acknowledgments

IPViseu, Vinícola Quinta da Neve and Vinícola Família Lemos de Almeida for all support

8PYCheM
Portuguese Young Chemists Meeting
17-19 May 2023 Vila Real

SYNTHESIS OF AMINO ACID-BASED SURFACTANTS THROUGH THE VALORISATION OFUSED COOKING OILS

Margarida I. M. Esteves[1*], César A. Henriques[2], Filipe E. Antunes[1,3]

[1]CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal; [2]EcoXperience, HIESE, Quinta Vale do Espinhal, Penela 3230-343, Portugal; [3]Science 351, IPN - Instituto Pedro Nunes, Edifício C, Coimbra 3030-199, Portugal. *margaridaimesteves@outlook.pt

The improper disposal of used cooking oils (UCO) has a negative impact on the environment. It is of utmost importance to properly discard UCO and explore sustainable solutions, such as recycling into value-added products, to minimize the ecological damages. [1]

The use of UCOs as a raw material for surfactant production is becoming an increasingly popular strategy for producing sustainable and environmentally friendly products. One approach to produce surfactants from UCO is their combination with amino acids, which are natural building blocks. The amino acids most commonly used for surfactant synthesis are sarcosine, lysine, and arginine. These amino acids can origin anionic, cationic or amphoteric surfactants, depending on the reaction conditions. [2]

A process for the synthesis of surfactants from UCO and amino acids involves the following steps: transesterification of triacylglycerides from UCO, neutralization of the amino acid and amidation reaction [3]. In this context, various amino acid-based surfactants **4** were synthesized, by studying the enzymatic amidation reaction with Novozym 435 (**figure 1**). Fatty acid ethyl ester (FAEE) **2** was obtained through the reaction of triacylglycerides **1** with ethanol, in the presence of calcium borohydride. The preparation of the targeted amino acid-based surfactants **4** was explored using sarcosine, lysine, and arginine (amino acids **3**), in neutral or salt form. The enzymatic amidation reaction of FAEE **2** and amino acids **3,** in the presence of Novozym 435, resulted in the successful synthesis of various surfactants **4**, with a lower carbon footprint and improved properties. In this communication, details of this study are provided.

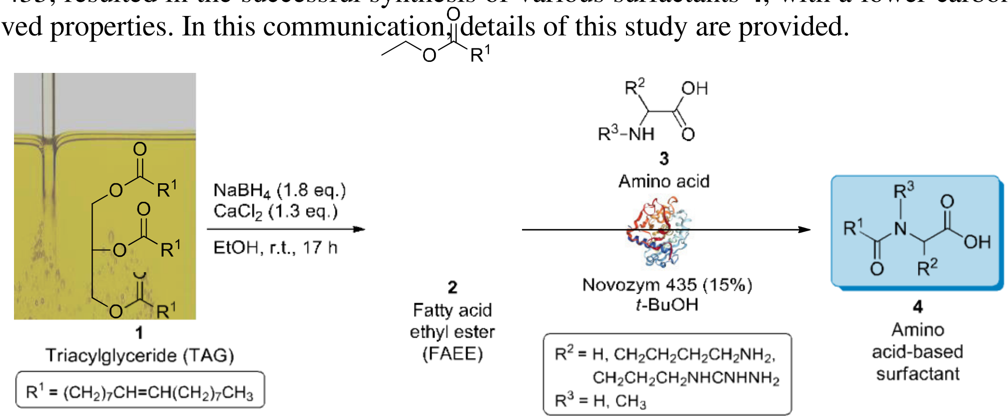


Figure 1: Synthetic pathway to amino acid-based surfactants derived from triacylglycerides of the used cooking oil.

References

[1] J. Cárdenas, A. Orjuela, D. L. Sánchez, P. C. Narváez, B. Katryniok, J. Clark, Journal of Cleaner Production, 289 (2021) 125129. [2] K. P. Ananthapadmanabhan, Tenside Surfactants Detergents, 56 (2019) 5.
[3] R. Valivety, P. Jauregi, I. Gill, E. Vulfson, Journal of the American Oil Chemists' Society, 74 (1997)7.

Acknowledgments

Thanks are due to Coimbra Chemistry Centre of the Institute of Molecular Sciences (CQC-IMS), supported by the Portuguese Agency for Scientific Research, "Fundação para a Ciência e a Tecnologia" (FCT). Margarida I. M. Esteves (PhD grant 2021.06758.BD) also thank FCT for funding. The authors also acknowledge the UC-NMR facility for obtaining the NMR data (www.nmrccc.uc.pt). And also acknowledge to "ECOSORV" project (CENTRO-01-0145-FEDER-181236), led by ECOXperience, LDA. in partnership with Institute Pedro Nunes and Active Aerogels, LDA.

EXTRACTION OF BIOACTIVE COMPOUNDS FROM GRAPE POMACE USING DEEP EUTECTIC SOLVENTS

Cátia Ferreira[1*], Manuela M. Moreira[2], Cristina Delerue-Matos[2], Mafalda Sarraguça[1]

[1] REQUIMTE/LAQV, Laboratório de Química Aplicada, Faculdade de Farmácia da Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal *up202102809@ff.up.pt
[2] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, R. Dr. António Bernardino de Almeida 431, 4249-015 Porto, Portugal

The cosmetic industry is one of the main producers of plastic packaging and toxic solvent residues. Over the last decade, there has been a huge evolution in the development of new environmentally friendly cosmetic ingredients. Thus, it is important to go back to the beginnings of the cosmetics industry using all the benefits of nature and its products. Deep eutectic solvents (DESs) have emerged as an alternative to the toxic solvents commonly used in the cosmetic industry. They are considered green solvents when they are made of natural compounds such as sugars, amino acids and organic acids [1]. They are simple to prepare, have an atom economy of 100% and hold unique physical and chemical properties such as a high solubilizing power for a wide range of natural compounds, a low vapor pressure and a high thermal stability and high viscosities and densities [1]. They are generally considered non-toxic, biodegradable and economic [2]. All these characteristics give them a great potential for application in the cosmetic industry. The use of bioactive compounds in cosmetic products implies their extraction from a natural raw material through energy and waste efficient green processes using a green solvent [3]. Subcritical DESs assisted extraction meets the above requirements. In the present work, DESs composed of different combinations of sugars, organic acids, amino acids, alcohols, water and others were used for the extraction of bioactive compounds from grape pomace using subcritical water extraction. The extracts were studied for their antioxidant properties using ABTS radical scavenging capacity assay and their reducing power by the ferric reducing antioxidant power (FRAP) assay. Additionally, the total phenolic content was determined by the Folin-Ciocalteu colorimetric method, the total monomeric anthocyanin content was determined by the pH differential method and the tannins content was determined by the precipitation method with methylcellulose. Globally, the DESs glycerol/tris/water (4:1:2), glycerol/tris/water (5:1:2) and glycerol/potassium carbonate (5:1) were found to perform best for the extraction of bioactive compounds from grape pomace.

References

[1] A. Tracy, G. Hélène, F. Sophie. Basics and properties of deep eutectic solvents: a review. Environmental Chemistry Letters 360 (2021) 119524.
[2] S. Madhur, K. Vaishnu, C. Mansi. A mini review on synthesis, properties and applications of deep eutectic solvents. Journal of the Indian Chemical Society 98 (2021) 100210.
[3] C. Farid, A. Maryline, F. Anne, S. Jochen, U. Lukas, G. Veronika, C. Giancarlo. Green extraction of natural products. Origins, current status, and future challenges. Trends in Analytical Chemistry 118 (2019) 248-263.

Acknowledgments

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. Mafalda Sarraguça thank FCT (Fundação para a Ciência e Tecnologia) for funding through program DL 57/2016 – Norma transitória. Manuela M. Moreira thanks FCT for funding through the Individual Call to Scientific Employment Stimulus (CEEC-IND/02702/2017).

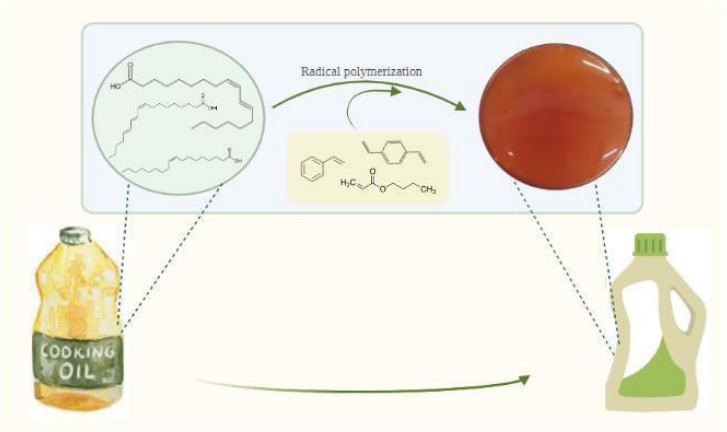
BIOPLASTICS FROM USED COOKING OIL

Inês C. P. Escobar[1*], Margarida I. M. Esteves[1]; César A. Henriques[2], Filipe E. Antunes[1 3], Jorge J. Coelho[4]

[1]CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal; [2]EcoXperience, HIESE-Quinta Vale do Espinhal, 3230-343 Penela, Portugal; [3]Science351, Instituto Pedro Nunes, Rua Pedro Nunes C, 3030-199 Coimbra, Portugal; [4]Department of Chemical Engineering, University of Coimbra, 3030-790 Coimbra, Portugal.
*ie.carolina@hotmail.com

Currently, approximately 800,000 tons of waste oil are improperly disposed of in the environment each year [1], affecting water quality and complicating the work of ETARs. Therefore, it is becoming increasingly important to develop strategies to reduce the environmental impact and combine this with the reuse of these wastes [2,3]. On the other hand, the development of polymeric materials that are more environmentally friendly is of great interest, especially when these materials come from renewable sources. Vegetable oils are considered as one of the most important classes of renewable sources, since they represent an interesting alternative for the chemical industry due to the large number of possible chemical modifications and the low price [4].

The main objective of this work was to valorize used cooking oil to make it a sustainable raw material for the production of new products with ideal properties that can be used in the packaging industry (Scheme 1). The use of fatty acids isolated from used oil (FAUO) proved to be more advantageous. Through a radical polymerization process with styrene, divinylbenzene and butyl acrylate, it was possible to obtain a polymeric matrix containing 37.5% FAUO. The results obtained with FAUO were compared with the use of acrylated epoxidized soybean oil (AESO) by thermal studies such as TGA, DSC and DMTA.



Scheme 1.

References

[1] Louzides, M. I.; Loizidou, X. I.; Orthodoxou, D. L; Petsa, D. Circular Bioeconomy in Action: Collection and Recycling of Domestic Used Cooking Oil through a Social, Reverse Logistics System. *Recycling* **2019**, 4 (2). https://doi.org/10.3390/recycling4020016.

[2] Crivello, J. V.; Narayan, R. Epoxidized Triglycerides as Renewable Monomers in Photoinitiated Cationic Polymerization. *Chem. Mater*. **1992**, 4 (3), 692-699. https://doi.org/10.1021/cm00021a036.

[3] Firdaus, M.; Meier, M. A. R. Renewable Co-Polymers Derived from Vanillin and Fatty Acid Derivatives. *Eur. Polym. J*. **2013**, 49 (1), 156-166. https://doi.org/10.1016/j.eurpolymj.2012.10.017.

[4] Ronda, J. C.; Lligadas, G.; Galià, M.; Cádiz, V. Vegetable Oils as Platform Chemicals for Polymer Synthesis. Eur. J. Lipid Sci. Technol. 2011, 113 (1), 46-58. https://doi.org/10.1002/ejlt.20100010

FORMALDEHYDE EMISSIONS IN WOOD-BASED PANELS – RELATIONSHIPS BETWEEN TEST METHODS

Margarida L. Almeida[1,2*], Cristina Coelho[1,2], Jorge M. Martins[1,2], Rui Miguel Ramos[3], Fernão Magalhães[4], Luísa Hora Carvalho[1,2]

[1]Wood Engineering Department, ESTGV – Polytechnic Institute of Viseu, Av. Cidade Politécnica, 3504-510 Viseu, Portugal; [2]LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; [3]LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, Porto, 4169-007, Portugal; [4]FEUP-Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. *malmeida@fe.up.pt

Formaldehyde (FA) is a chemical compound classified as carcinogenic and toxic. It is a colourless, pungent-smelling gas and its presence in indoor air is harmful to human health. Sources include environmental tobacco smoke and other combustion sources; pressed wood products – such as particleboard and certain textiles, foams and glues [1].

The wood-based panels (WBP) industry uses mainly formaldehyde-based resins, such as: urea-formaldehyde (UF), melamine-formaldehyde (MF) or melamine-urea-formaldehyde (MUF), due to its low cost, fast curing and good mechanical properties [2].

For the determination of FA release in WBP, there are different test methods available, following European standards, such as: chamber method – EN 717-1, gas analysis method - EN ISO 12460-3, flask method - EN 717-3 and perforator method - EN ISO 12460-5. The desiccator method, determined by the Japanese standard JIS A 1460, is also used.

A major problem when comparing different FA standards, is the different properties being measured as some methods measure the FA emission in WBPs - EN ISO 12460-3, while others measure its content - EN ISO 12460-5. The correlation between results from different methods has been a matter of debate, not yet completely elucidated [3].

With this in mind, the objective of this work was to establish regression models between two methods already existing in European standards – EN ISO 12460-3 and EN ISO 12460-5, in order to validate their future use. For this work, several tests were performed applying both methods to the same sample of industrially produced dry-process fibreboard - coloured MDF (Medium Density Fibreboard). A big issue in this study is the impact of unrelated properties such as thickness, density, moisture content, colour of MDF on the relationship between formaldehyde emission (FE) and formaldehyde content (FC). So, the samples collected represent a wide range of values for those properties, including black, brown, grey, yellow, orange, red, green, blue as colours and 8, 10, 12, 16, 19, 30 mm as thicknesses.

References

[1] U.S. Environmental Protection Agency, (2012). An introduction to indoor air quality (IAQ). Volatile organic compounds (VOCs). Washington, DC: U.S. EPA.

[2] Dunky, M., Urea–formaldehyde (UF) adhesive resins for wood. International Journal of Adhesion and Adhesives, (1998), 18(2): p. 95-107.

[3] Carvalho, L., F. Magalhães, and F. João, Formaldehyde Emissions from Wood-Based Panels -Testing Methods and Industrial Perspectives. 2012

Funding

This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE), funded by national funds through FCT/MCTES (PIDDAC); project PTDC/CTM-PAM/1348/2021 funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES.

Acknowledgments

RMR tanks FCT (Fundação para a Ciência e Tecnologia) for funding through program CEECIND/04259/2017.

P28

STUDY OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL BY ETHYL TRANSESTERIFICATION AND ITS PURIFICATION WITH THE USE OF ACTIVATED CARBONS DERIVED FROM OLIVE PITS

Gabriel L. Camilo,[1,2*] Ana Queiroz,[1,2] António E. Ribeiro,[1,2] Maria Carolina Sérgi Gomes,[3] 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]Universidade Tecnológica Federal do Paraná (UTFPR-AP), 86812-460 Apucarana, PR, Brasil. *glaminocamilo@gmail.com

The world production of biodiesel in 2020 reached approximately 46 million tons, with 10% of the total amount representing biodiesel from waste cooking oils (WCO) [1]. The cost of conventional biodiesel production is higher than of diesel from petroleum, since it is carried out 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 to help address global renewable energy challenges [3]. The wet washing method, which uses water to purify the esters, is the most commonly used purification process in biodiesel production. Despite being an efficient method, wet washing generates huge amounts of wastewater, on the other hand, dry washing methods uses an appropriate adsorbent to selectively adsorb certain impurities from the liquid phase onto its surface, avoiding the use of water in the purification step and offering several advantages, including simple integration into an existing industrial plant, shorter purification time and lower effluent generation.

In this work, the goal is to optimize the production of biodiesel from WCO via the ethylic route through its purification by adsorption with a focus on glycerol removal, applying various natural adsorbents, physically and chemically activated with acid and basic agents, and obtained from residual sources of biomass (olive pits). The optimized conditions for the production of biodiesel were found using a response surface methodology with 3 parameters: alcohol/oil molar ratio, reaction temperature and catalyst concentration. Four types of activated carbon were produced from the same precursor (olive pits) and then characterized. The two most efficient materials for glycerol removal were selected by means of equilibrium adsorption studies. Afterwards, kinetic adsorption batch studies (see Table 1) were carried out at 3 different temperatures for each of the two selected adsorbents (CA-800°C and CA-$ZnCl_2$) using the same adsorbent concentration (5% wt/wt). The dry washing proved to be efficient in drastically reducing water consumption and effluent generation, in addition, an energy consumption reduction is achieved since there is no need to heat the biodiesel to remove moisture caused from the wet washing process.

Table 1: Adsorption kinetic results using 5% (wt/wt) of adsorbent.

Adsorbent	Temperature (°C)	Removal (%)	q_e (mg/g)
CA-800°C	25	62.6%	32.0
	35	66.1%	31.9
	45	68.8%	34.7
CA-$ZnCl_2$	25	73.7%	33.5
	35	78.7%	33.8
	45	79.8%	38.7

References

[1] JOPA, Data from ISTA Mielke's Oil World Annual Report and Other Editions, Japan Oilseed Processors Association (JOPA), Tokyo, 2020, https://www.oil.or.jp/kiso/seisan/seisan03_02.html (Accessed April 14, 2022).
[2] R. Ahmed, K. Huddersman, Journal of Industrial and Engineering Chemistry, 110 (2022) 1.
[3] C. Chen, A. Chitose, M. Kusadokoro, H. Nie, W. Xu, F. Yang, S. Yang, Energy Reports, 7 (2021) 4022.

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/0007/2021).

P29

VALORIZATION OF OLIVICULTURE RESIDUES FOR THE REMOVAL OF ESTROGENS FROM WATER

Eduardo C. Milani[1,2,3*], Maraísa L. Menezes[3], Jose L. Diaz de Tuesta[4], 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 (SusTEC), 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. *eduriqueerick@gmail.com

Estrogens belong to the class of water micropollutants named as endocrine disrupting chemicals and are considered persistent substances in the environment. Estrogens are a type of hormones that are continuously released to environment presenting several undesirable effects on aquatic species and human health even when present at very low concentrations (trace levels) [1, 2]. Additionally, it is known that traditional sewage and drinking water treatment plants are not able to remove or degrade these compounds and additional treatments are required [3, 4]. Currently, there is an effort to produce bio-based adsorbents that are able to remove efficiently a wide range of micropollutants from water [5]. With the present work we will present an extensive set of experimental results that presents the valorization of olive stones residues to prepare activated carbons to be used as adsorbent for the removal of estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) by adsorption from water. Five different adsorbents were produced, namely powdered olive stone (OS), physical activated at 800°C (CF), carbonized at 500°C (CC), chemical activated using phosphoric acid (CA) and chemical activated with sodium hydroxide (CB). The carbonization yield was calculated and the pH at point of zero charge (pH$_{PZC}$), BET surface area (S$_{BET}$) of the carbonaceous materials were determined (see **Table 1**). The simultaneous removal of the three estrogens (E1, E2 and EE2) from water was evaluated for all the five prepared adsorbents. For the adsorbent with the best removal performance, a kinetic study was also carried out. The obtained results show that olive stones exhibit potential for the production of ACs with high surfaces used to remove estrogens from water.

Table 1: **Surface properties and estrogen removal in olive stone adsorbents.**

Adsorbents	Yield (%)	pH$_{PZC}$	S$_{BET}$ (m^2/g)	Total estrogen removal (%)
OS	-	5.43	4	24.2
CF	23.0	8.64	14	24.9
CC	26.9	8.46	67	51.2
CA	57.5	3.84	590	96.4
CB	33.9	8.92	27	36.6

References

[1] P. Bhatt et al., J Environ. Chem. Eng. 10 (2022) 107598.
[2] Daniela Guerrero-Gualan et al., Water 15 (2023) 353.
[3] M. Gavrilescu et al., New Biotechnol. 32 (2015) 147.
[4] F. Fadzail et al., Materials Today: Proceedings. 57 (2022) 1108.
[5] Jose L. Diaz de Tuesta et al., J. Environ. Chem. Eng. 9 (2021) 105004.

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/0007/2021). J.L. Diaz De Tuesta acknowledges the financial support of "Comunidad de Madrid" (Spain) for the individual research grant 2020-T2/AMB-19836.

EXPLORING THE SYNERGIES OF 3D-PRINTED BIOCHAR-INORGANIC POLYMER COMPOSITE AS AN EFFECTIVE CO_2 ADSORBENT

Inês Correia[1*], Nuno P.F. Goncalves[1], Marina Ilkaeva[1], Rui M. Novais[2], Luís Mafra[1], Mirtha A.O. Lourenço[1]

*[1]University of Aveiro, Chemistry Department, CICECO, Aveiro, Portugal; [2]University of Aveiro, Department of Materials and Ceramic Engineering, CICECO, Aveiro, Portugal; *ines.p.correia@ua.pt*

Extensive research has been conducted on the impact of greenhouse gas emissions on the environment, particularly regarding global climate change. Among the gases contributing to this phenomenon, CO_2 is the most significant, largely due to its high production through fossil fuel combustion. To address these concerns, there has been an enormous interest in developing CO_2 capture and storage technologies. One promising avenue is using biochars as CO_2 adsorbents, which are derived from the pyrolysis of waste materials and biomass. These materials possess tailored textural properties and can be produced sustainably through various pyrolysis conditions and feedstocks.[1]

Porous inorganic polymers, such as those derived from red mud, a waste product of alumina production, have also gained attention due to their environmental potential as effective sorbents.[2] These polymers exhibit significant CO_2 adsorption capacity, compressive strength, regeneration performance, and are interesting due to their low energy impact during the manufacturing process.[3] New technologies, such as additive manufacturing, have enabled the preparation of porous inorganic polymers with more controlled pore morphology and increased open porosity.[4]

To explore the synergies between these two materials, we have investigated the development of a 3D-printed CO_2 adsorbent composed of biochar and inorganic polymer. The study examined the impact of different heating methods and pyrolysis temperatures on the characteristics and adsorption behavior of the chitosan-derived biochar. Furthermore, we have explored the possibility of creating a 3D-printed composite by combining the best-performing biochar with red mud-containing inorganic polymer.

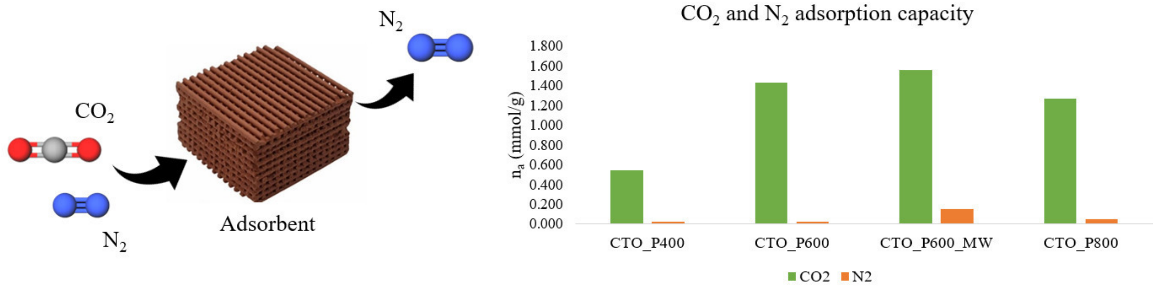


Figure 1: 3D-printed biochar-inorganic polymer composite for CO_2 removal (left); CO_2 and N_2 adsorption capacity results of biochar (right).

References
[1] P. D. Dissanayake et al., Renewable and Sustainable Energy Reviews, 109582, 124, 2020.
[2] A. Sattari, et al., Journal of CO2 Utilization, 101526, 48, 2021.
[3] A. L. Freire et al., J Clean Prod, 122917, 273, 2020.
[4] C. Bai and P. Colombo, Ceramics International, 44, 2018, 16103–16118.

Acknowledgments
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/MEC (PIDDAC). This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement 865974). FCT is also acknowledged by MAOL. and MI for a Junior Researcher Position (CEECIND/01158/2021 and CEECIND/00546/2018, respectively). NG and MAOL. further acknowledge funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie PF grant agreement No 101065059 and No 101090287, respectively. R.N. acknowledges the financial support of the FCT project MAXIMUM (PTDC-CTM-CTM-2205-2020).

IRON NANOFERTILIZERS FOR THE DEVELOPMENT OF SUSTAINABLE SOYBEAN CROPS

Simão Pinho[1,2], Carla Santos[1], Maria Rangel[3], Marta Vasconcelos[1], Salette Reis[2], Tânia Moniz[2,3,4]

[1]CBQF, Centro de Biotecnologia e Química Fina, Universidade Católica Portuguesa, Edifício de Biotecnologia, Rua de Diogo Botelho, 1327, 4169-005 Porto, Portugal;
[2] LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal;
[3]LAQV, REQUIMTE, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal;
[4]LAQV, REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, s/n 40169-007 Porto, Portugal.

Nowadays, about 30% of the world's arable land is composed of calcareous alkaline soils, which causes iron deficiency chlorosis in certain crops, having the potential to influence crop yields in a negative way [1]. The aim of this study is to create nanofertilizers, as nanoparticles carrying iron chelates, namely 3-hydroxy-4-pyridinones (3,4HPO) iron(III) chelates, which have shown to be effective in reducing chlorosis in *Glycine Max* (soybean) plants in previous studies [1], and can be used to treat affected plants, by providing a necessary supply of iron to chlorotic plants, and releasing it in a controlled and sustainable rate.

The initial part of this work consisted of the production, optimization and characterization of different formulations of polymer-based nanoparticles, varying in size, and labeled with a fluorescent marker (rhodamine B). These formulations were tested in 2 weeks grown *Glycine max* plants to access the potential differences in their uptake (**Figure 1**), with the purpose of choosing the best formulation to carry out the future studies considering the iron chelates loaded nanoparticles. Confocal fluorescent microscopy was used to investigate the absorption profile, revealing the potential of medium-sized nanoformulations, due to their notable presence in the stem (**Figure 2**) and leaves of the plant.

Figure 1: *Glycine Max* plants exposed to different rhodamine B labeled nanoparticles.

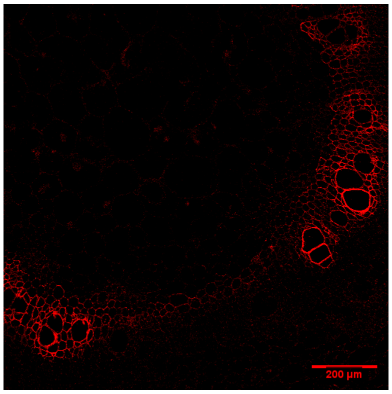


Figure 2: Traces of rhodamine B in the stem of a plant treated with medium-sized nanoparticles.

References

[1] Santos, C. S., Rodrigues, E., Ferreira, S., Moniz, T., Leite, A., Carvalho, S. M. P., Vasconcelos, M. W. and Rangel, M. (2021). Foliar application of 3-hydroxy-4-pyridinone Fe-chelate [Fe(mpp)3] induces responses at the root level amending iron deficiency chlorosis in soybean, Physiologia Plantarum, 1-11. Doi: 10.1111/ppl.13367

Acknowledgments

Financial support from PT national funds (FCT/MCTES): UIDB/50006/2020, UIDP/50006/2020 and EXPL/QUI-QIN/0411/2021.

CEFTRIAXONE-LOADED LIPID NANOPARTICLES TO TREAT PROSTHETIC JOINT INFECTIONS CAUSED BY *S. AUREUS*

Daniela R. P. Loureiro,[1,2,3] Catarina L. Seabra,[3] José X. Soares,[3] Amber De Bleeckere,[4] Tom Coenye,[4]
Cláudia Nunes,[3] Carlos M. M. Afonso,[1,2] Salette Reis,[3*]

[1] Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.
[2] Interdisciplinary Center of Marine and Environmental Investigation (CIIMAR/CIMAR), Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Porto, Portugal.
[3] LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.
[4] Laboratory of Pharmaceutical Microbiology (LPM), Ghent University, Ottergemsesteenweg 460, 9000 Ghent, Belgium.
*shreis@ff.up.pt

The number of joint replacement surgery increased in the last years, in combination with a constant infection rate of 1%–3%, leading to a high number of prosthetic joint infections (PJI). [1] PJI are often resulting from biofilms and *Staphylococcus aureus* is responsible for more than 50% of the cases. [2] Bearing in mind the significant morbidity and mortality associated with PJI, there is an urgent need for novel preventive and therapeutic approaches. [3] To address this problem, we proposed an innovative nanotherapy based on the encapsulation of an antibiotic in a lipid nanocarrier to target and disrupt the biofilm barrier. Ceftriaxone (CTX) is a third-generation cephalosporin with activity against *S. aureus*. However, CTX has poor cellular penetration resulting from the high molecular weight and the high hydrophilicity. To circumvent these drawbacks, this drug was encapsulated in the nanostructured lipid carrier (NLC). To guarantee the suitable physicochemical properties and a higher drug encapsulation, the nanoformulation was optimized by Machine Learning (ML). Moreover, the *in vitro* antibiofilm efficacy of the optimized CTX-loaded NLCs was tested using two different media: common laboratory media and media that closely mimicking the *in vivo* environment of PJI, namely, synovial fluid media. The antibiofilm activity was evaluated by metabolic activity of biofilm (by resazurin assay) and colony-forming unit (CFU) count. A significant reduction of metabolic activity of biofilm was assessed around 90 % using the CTX-loaded NLC against *S. aureus* biofilms at concentration 125 μg/mL. CTX-loaded NLC reduced the bacterial load by ~6 $\log_{10}$ for 250 μg/mL. These findings suggest that the optimized CTX-loaded nanoparticles present a potential therapeutic approach against PJI caused by *S. aureus*.

References

[1]. Stamm, J., et al., Development of an artificial synovial fluid useful for studying Staphylococcus epidermidis joint infections. Front Cell Infect Microbiol, 12 (2022) 948151.
[2]. Bidossi, A., et al., Identification and Characterization of Planktonic Biofilm-Like Aggregates in Infected Synovial Fluids From Joint Infections. Front Microbiol, 11 (2020) 1368.
[3]. Izakovicova, P., O. Borens, and A. Trampuz, Periprosthetic joint infection: current concepts and outlook. EFORT Open Rev., 4(7) (2019) 482.

Acknowledgments

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. Daniela R. P. Loureiro thanks FCT for her PhD grant (SFRH/BD/140844/2018)

P33

BIOPOLYMERS AS SHELL MATERIALS FOR MICROCAPSULES

Cátia S. M. Esteves[1*] Filipe E. Antunes[1,2]

[1]Coimbra Chemistry Centre, Department of Chemistry, Institute of Molecular Sciences (IMS), Faculty of Sciences and Technology, University of Coimbra, 3004-535 Coimbra, Portugal [2]Science 351 - Disruptive & Sustainable R&D Innovations, IPN - Instituto Pedro Nunes, Edifício C, Coimbra 3030-199, Portugal *csmesteves@gmail.com

Encapsulation-based self-healing technology is used in many fields to preserve the properties of the material. One of the applications is the encapsulation of healing agents for coatings. When a polymeric coating is damaged, the presence of healing agents at the site of the crack serves to repair the barrier and extend the life of the coating. However, if healing agents are directly incorporated into the coating, they can lose effectiveness over time and react with corrosive species, such as oxygen and moisture, even when damage does not occur. The alternative to overcome these problems can be done by using microencapsulation. With this technology, it is possible to improve the long-time efficiency of the core, promote stabilization against environmental degradation and allow its release in a controlled manner [1].

Several studies have been published using dicyclopentadiene, oils, epoxy and alkyd resins, mercaptan, and isocyanates, among others, as core components of microcapsules. Of these, oils are of interest because they react with oxygen, oxidize, and form a film that can seal the defects of the polymeric matrix [2]. Urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, and styrene co-acrylonitrile are the most commonly used combinations of polymers that serve as shell. However, toxic components are used in the production of these polymers. For this reason, the search for sustainable alternatives is necessary, such as the application of biopolymers [3]. The use of biopolymers with high biocompatibility, biodegradability, and sustainability, is increasingly being explored as a possible alternative to synthetic polymers in microencapsulation.

In this work, we present new microcapsules with polycaprolactone (PCL) and polylactic acid (PLA) as shell and linseed oil as healing agent in the core, for application against corrosion. Different solvents were used to prepare these new microcapsules, and the effects of stirring speed and reaction time were also studied.

References

[1] S. M. Mirabedini, I. Dutil, R. R. Farnood, Colloids and Surfaces A, 394 (2012) 74-84
[2] I. Amazian, S. R. Allahkaram, S. Rezaee, Royal Society of Chemistry, 12 (2022) 14299-14314
[3] G. K. Çömlekçi, S. Ulutan, Progress in Organic Coatings, 121 (2018) 190-200

Acknowledgments

The authors are thankful to Coimbra Chemistry Centre (CQC-IMS), supported by the Portuguese Agency for Scientific Research, FCT. Cátia S. M. Esteves acknowledges FCT for PhD grant (2020.04911.BD).

DEPOSITION OF H-LUMNO$_3$ THIN FILMS BY MOCVD: GROWTH AND STRUCTURAL CHARACTERIZATION

A.A. Bassou[1], J.R. Fernandes[1], F.G. Figueiras[2], P.B. Tavares[3]

[1] CQVR, Physics Dep., ECT, Univ. Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal.;
[2] IFIMUP, Physics and Astronomy Dep., Fac. Ciências da Univ. Porto, 687, 4169-007 Porto, Portugal.;
[3] CQVR, Chemistry Dep, ECVA, Univ. Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal;
* abderrazzak@utad.pt

The interest in advanced functional materials is globally increasing, particularly in the field of photocatalysis and photovoltaic applications. One of the most interesting materials for this type of application is the rare earth manganites ($ReMnO_3$). These systems have been widely studied both as polycrystalline ceramics and as single crystals [1]. Thin films present additional degrees of freedom to explore, like substrate induced strain and interface modifications, opening practical pathways for designing multifunctional devices. Several physical-based techniques can be used to prepare thin films, such as pulsed laser deposition [1] or RF Magnetron Sputtering. On the other hand, chemical methods have the advantage of comparative low cost, providing versatility on precursors composition and thus prompt control of films stoichiometry. In particular, the metal organic chemical vapor deposition (MOCVD) method allows to investigate a series of relevant parameters in order to establish the suitable deposition conditions to deposit $ReMnO_3$ thin films.
In this study, we explore MOCVD conditions targeting to deposit thin films with the hexagonal $LuMnO_3$ phase as a potential low band gap ferroelectric material. Main parameters investigated are metalorganic precursors ratios, substrate temperature and annealing effect. The work uses two different substrates, platinized silicon (Si(100)/SiO_2/TiOx/Pt) and silica glass (SiO_2). To investigate the thermodynamic stability and quality of the developed phases, a detailed analysis of the films crystal structure, microstructure, morphology, and roughness were carried out by X-ray diffractometer, scanning electron microscopy (SEM), Energy Dispersive Spectrometry (EDS), Raman spectroscopy and piezo force microscopy (PFM). The results revealed the relevance of deposition temperature and precursors composition molar ratio as critical parameters to grow *P6₃cm* *h*-$LuMnO_3$ phase. It was found that formation of the *h*-$LuMnO_3$ single phase can be obtained within a window $0.93 < |Lu|/|Mn| < 1.33$ of the film composition. Moreover, the XRD patterns indicate that amorphous films deposited at 700 °C become crystalized after *ex-situ* annealing at 800 °C in air or in argon. Optimization of deposition conditions and *in-situ* annealing for long periods further improves the quality of the film. These films display a relatively narrow band gap (Figure 1) around 1.5 eV within the values reported for the *h*-$LuMnO_3$ system [2] which is considered to be the best value for photovoltaic applications.

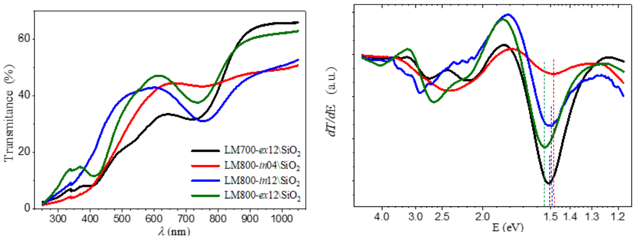


Figure 1: *h*-$LuMnO_3$ films on SiO_2 substrates (left) transmittance and its derivative (right)

References
[1] A.M. Zhang, H.F. Cao, X.X. Pan, J.J. Zhu, X. S. Wu, Thin Solid Films 750, 2022, 139186.
[2] Y. Sheng, I. Fina, M. Gospodinov, J. Fontcuberta, Appl. Phys. Lett. 118, 2021, 232902.

Acknowledgment: The authors would like to acknowledge Fundação para a Ciência e Tecnologia (FCT) through projects CERN/FIS-TEC/0003/2019 and CERN/FIS-NUC/0003/2021. Project Obtain NORTE-01-0145-FEDER-0000084. UIDB/QUI/00616/2020. A special acknowledgment is made to UME/UTAD for SEM/EDS and XRD measurements.

THE DIALYSIS EFFECT: INSIGHTS ON THE ROLE OF PURIFICATION PROCESSES IN THE PROPERTIES OF CARBON NANOMATERIALS

Andreia D. Veloso,[1*] Romeu A. Videira[2], Maria Cristina Oliveira,[1]

[1] Chemistry Center – Vila Real (CQ-VR), Chemistry Department, School of Life and Environmental Sciences, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal; [2] REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal.*andreiaveloso8@hotmail.com

Dialysis is typically addressed in the post-synthesis treatment of nanomaterials to eliminate the precursors and/or undesirable side products that occur naturally during their synthesis. Usually, it is assumed that this purification process does not affect the nanomaterial structure. However, it has been shown that some nanomaterials properties can be lost after this purification step, like the optical properties of carbon dots synthesized via a bottom-up methodology [1]. Top-down approaches, like the electrochemical generation of carbon nanoparticles from graphite, may not lead to side products but require a separation procedure, like dialysis, to remove the electrolyte from the electrolytic solution.

On account of the singular properties exhibited by as-prepared carbon-based nanomaterials synthesized electrochemically from carboxylic buffers [2], this work aims to evaluate if the dialysis process can affect their properties, mainly their redox and optical properties. Additionally, a systematic investigation of the structural properties of the carbon nanomaterial before and after the dialysis process is carried out to understand how the putative structural alterations triggered by the dialysis process affect the functionality of nanomaterials and their spectrum of applications. The redox behavior is assessed by cyclic voltammetry and the optical properties are characterized by UV-Visible absorbance and fluorescence spectroscopy. The structural properties of the nanomaterial are followed by ATR-FTIR, ^{1}H RMN, and ^{13}C NMR spectroscopy. The results revealed that the electrolyte removal by the dialysis process induces structural changes in carbon-based nanomaterials along with changes in their properties.

References

[1] J.B. Essner, J.A. Kist, L. Polo-Parada, G.A. Baker, Chemistry of Materials, 30 (2018) 1878.
[2] A.D. Veloso, R.A. Videira, M.C. Oliveira, Electrochimica Acta, 404 (2022) 139734.

Acknowledgments

Fundação para a Ciência e Tecnologia (SFRH/BD/138425/2018, UIDB/00616/2020, UIDP/00616/2020, UIDB/50006/2020) and NORTE2020 (project OBTAIN, NORTE-01-0145-FEDER-000084).

PRODUCTION OF ECO-MATERIALS FROM FOREST RESIDUES TO REPLACE CONVENTIONAL PLASTICS

Carolina F. Jesus,[1*] Francisco J.P.M. Sousa,[1] Filipe E. Antunes [1,2]

[1] Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal;[2]Science351, Instituto Pedro Nunes, Rua Pedro Nunes C, 3030-199 Coimbra, Portugal.*carolinaajesus@gmail.com

The development of biocomposites to replace non-biodegradable plastics for the production of disposable products is critical due to exponential growth since 1950. In 2021, the production of conventional plastics will reach 390.7 million tons, so there is an urgent need to replace them. However, simply replacing plastics with biopolymers does not make it possible to obtain materials with the same properties as conventional polymers, apart from the fact that biopolymers still have a high cost [1].To improve material properties and reduce production costs, reinforcing elements based on natural fibers such as sawdust, cork, and microcrystalline cellulose are used to synthesize composites to overcome the limitations of isolated biopolymers [2, 3, 4]. This work aims to respond to the growing need to reduce the presence of non-biodegradable plastics and replace these materials with eco-composites that can be converted into various end products, while maintaining or adapting conventional processing technologies to produce plastic articles. To achieve this, the Bioflex matrix was incorporated with varying concentrations of eucalyptus and pine sawdust, cork, and microcrystalline cellulose. Then the new biomaterials were assessed for their water absorption, solubility, and mechanical properties. The results obtained indicate strong compatibility between the fibers and the polymeric matrix. This leads us to the possibility of replacing conventional plastics with the ones obtained.

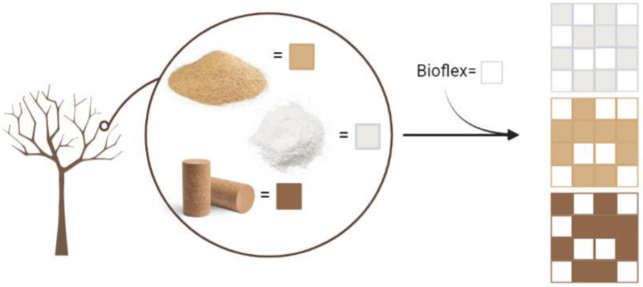


Figure 1: Production of new sawdust and cork-based eco-materials.

References
[1] Gil, L. (2009). Cork composites: a review. Materials, 2(3), 776-789.
[2] Fernandes, E. M., Correlo, V. M., Mano, J. F., & Reis, R. L. (2015). Cork–polymer biocomposites: Mechanical, structural and thermal properties. Materials & Design, 82, 282-289.
[3] Hoyos, C. G., Cristia, E., & Vázquez, A. (2013). Effect of cellulose microcrystalline particles on properties of cement based composites. Materials & Design, 51, 810-818.
[4] Anbu, G., Manirethinam, N., Nitish, K. P., Pavithran, K., Priyadharsan, A., & Sabarigiri, S. (2019). Review of development of brake pads using sawdust composite. Journal of Critical Reviews, 7(4), 2020.

Acknowledgments
Authors thanks to PT2020 – Sistema de Incentivos à Investigação e Desenvolvimento Tecnológico (SI I&DT) Aviso Nº 17/SI/2019. This work was developed within the scope of the project Ecoplast - Eco-Sustainable composite materials to replace conventional plastics, with the reference POCI-01-0247-FEDER-069002 from the Portuguese National Innovation Agency.

BIOMASS-DERIVED (ELECTRO)CATALYSTS FOR SUSTAINABLE PROCESSES

Inês S. Marques,[1] Renata Matos,[1] Andreia F. Peixoto,[1] Diana M. Fernandes [1*]

[1]LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal. *diana.fernandes@fc.up.pt

The current energy crisis and war has been stimulating new measures to reduce energy consumption and chemical production from fossil resources. In this regard, the concept of biorefinery is an essential strategy to convert biomass residues into value-added products and energy [1]. Conventional (electro)catalysts are based on noble metals and their oxides, such as Pt, Pd, RuO_2, and IrO_2. Therefore, it is imperative to develop a new generation of high sustainable and stable materials based preferentially in biomass wastes to contribute to the circular environment and economic benefits [2].

Biochar, a carbon-rich and porous solid material obtained from thermochemical degradation of biomass can be a future alternative. The production of catalysts from natural and renewable sources - vineyard pruning waste (VPW) or shrimp shell waste (SSW) biochar - will be used for sustainable catalytic processes for value-added bioproducts and as electrocatalysts for demanding electrochemical reactions, oxygen reduction and evolution reactions (ORR and OER). In this project, we aim to produce nitrogen-doped supported metals and sulfonic acid-based catalysts to convert waste into wealth through innovative and potentially low-cost approaches. Biochar catalysts were prepared by wet impregnation or ball milling. The activation under chemical/physical experimental conditions resulted in high surface areas (BET > 200 m^2/g). The successful preparation of the functionalized catalysts was also verified by XPS, FTIR and SEM/EDS; the formation of highly porous structures was demonstrated by SEM and XPS resulting in a significant increase in N-functionalization after doping approach. The electrocatalysts demonstrated moderate ORR electrocatalytic performance in alkaline medium with diffusion-limiting current densities between -3.7 and -1.2 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 0.4 and 0.7 V vs. RHE and maximum current densities above 45 mA cm^{-2}. The catalysts showed remarkable yields such as: 88% of furfuryl alcohol from CTH reaction of furfural; and, up to 90 % of ethyl levulinate (EL) from 5-HMF using mild experimental conditions (130 °C and 6h reaction) using biochar functionalized with sulfonic acid [4,5].

References

[1] M.C. Gaspar, C.V.T. Mendes, S.R. Pinela, R. Moreira, M.G.V.S. Carvalho, M.J. Quina, M.E.M. Braga, A.T. Portugal, Assessment of Agroforestry Residues: Their Potential within the Biorefinery Context, ACS Sustainable Chemistry & Engineering, 7 (2019) 17154-17165.
[2] B. Bradić, U. Novak, B. Likozar, Crustacean shell bio-refining to chitin by natural deep eutectic solvents, Green Processing and Synthesis, 9 (2020) 13-25.
[4] I.S. Marques, B. Jarrais, R. Ramos, V.K. Abdelkader-Fernandez, A. Yaremchenko, C. Freire, D.M. Fernandes, A.F. Peixoto, Nitrogen-doped biochar-supported metal catalysts: High efficiency in both catalytic transfer hydrogenation of furfural and electrocatalytic oxygen reactions, Catalysis Today, (2023) 418.
[5] A.F. Peixoto, R. Ramos, M.M. Moreira, O. Soares, L.S. Ribeiro, M.F.R. Pereira, C. Delerue-Matos, C. Freire, Production of ethyl levulinate fuel bioadditive from 5-hydroxymethylfur-fural over sulfonic acid functionalized biochar catalysts, Fuel, (2021) 303.

Funding

This work was funded by Portuguese funds through Fundação para a Ciência e a Tecnologia (FCT/MCTES) in the framework of the project EXPL/BII-BIO/0436/2021.

Acknowledgments

Thanks, are also due to FCT for the projects UIDB/50006/2020, UIDP/50006/2020. D.M.F. and A.F.P. thank FCT for funding through the Individual Call to Scientific Employment Stimulus (Refs. 2021.00771.CEECIND/CP1662/CT0007 and 2020.01614.CEECIND/CP1596/CT0007 respectively). R.M. thanks FCT for the PhD fellowship 2020.05342.BD. I.S.M. thanks FCT for the fellowship contract in the framework of Project EXPL/BII-BIO/0436/2021.

AMINATED SILICA FROM RICE HUSK TOWARDS LUMINESCENT LANTHANIDE MATERIALS

Gabriela Coelho, Mariela M. Nolasco, Sofia M. Bruno*

Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal
*sbruno@ua.pt

Specific features namely luminescence can be provided by silica-based mesoporous materials functionalized with rare-earth elements such as europium [1]. Aminated silica from rice husk provides a sustainable matrix able to be functionalized to achieve a desirable application.

In this context, silica functionalization was provided by the immobilization of 3-Triethoxysilylpropyl 4-Pyridylacetamide and subsequent complexation with the europium dicarboxylate complex Eu(H_2nda)(bipy) [H_2nda = 2,6-naphthalenedicarboxilic acid; bipy = 2,2´-bipyridine] [2] .

The material was structurally and electronically characterized. The joint use of vibrational (DRIFT and Raman) and NMR spectroscopies, as well as thermal analysis (TGA/DSC) and electronic structure techniques (UV-vis and Photoluminescence) allow us to confirm the success in the synthesis of this new material. DFT and TD-DFT techniques were also applied to decipher the experimental results.

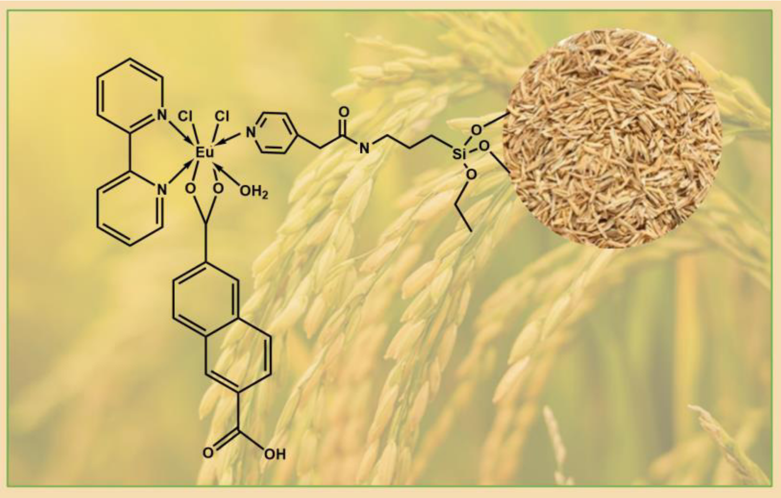


Figure 1: Europium based-aminated silica from rice husk

References
X. Author, Y. Author, Z. Author, Journal name, 20 (2001) 537.
[1] S. M. Bruno, A. C. Coelho, R. A. S. Ferreira, L. D. Carlos, M. Pillinger, A. A. Valente, P. Ribeiro-Claro, I. S. Gonçalves, Eur. J. Inorg. Chem., 24 (2008), 3786.
[2] M. R. Felício, Mário, P. D. Vaz, C. D. Nunes, M. M. Nolasco, New J. Chem., 46 (2022) 2131.

Acknowledgments
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). The STFC Rutherford Appleton Laboratory is thanked for access to neutron beam facilities (TOSCA/ RB2190096).

P39

HIGH PERFORMANCE ELECTROCATALYSTS DERIVED FROM SHRIMP SHELLS TOWARDS OXYGEN REDUCTION

Renata Matos,[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.
*diana.fernandes@fc.up.pt

The development of new alternatives to fossil fuels combustion has been a major research highlight in the last decades, with special focus being placed on energy conversion devices such as fuel cells and metal-air batteries. However, both technologies rely on several electrochemical processes, including the oxygen reduction reaction (ORR), whose sluggish kinetics and large overpotentials hinders their practical application [1]. These limitations can be overcome by the development of highly effective electrocatalysts. While currently Pt-based materials are considered the state-of-the-art electrocatalysts towards ORR, heteroatom-doped carbon catalysts arose as promising precious metal-free alternatives [2]. Recently, carbon materials obtained from the pyrolysis of biomass, known as biochars, have attracted interest as highly sustainable catalysts, due to their tunable physical-chemical properties, renewable feedstock, and low production cost [3]. Shrimp shells derived biochars, in particular, have very interesting electrocatalytic properties, originated from the feedstock natural abundance in heteroatoms [4].

Herein, carbon-based electrocatalysts were obtained from the pyrolysis of shrimp shell waste. In order to evaluate the effect of heteroatoms in the ORR performance, the most promising biochar was further doped with different sources of N and/or S through a solventless ball milling approach. Then, the doped biochars were functionalized with electroactive Co_3O_4 nanoparticles *via in situ* co-precipitation route (**Figure 1**). All the prepared materials were fully characterized prior to their use as ORR electrocatalysts. The resulting hybrid materials showed excellent electrocatalytic performance in alkaline medium, displaying faster kinetics and lower overpotentials compared with the original biochar. Although thesecatalysts still present more negative E_{onset} and lower j_L values than the state-of-the-art Pt/C, they displayed very similar selectivities towards the desired 4 electron reduction and even significantly lower Tafel slopes than Pt/C.

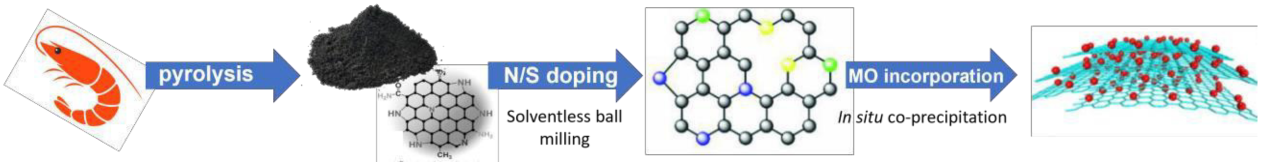


Figure 1: Preparation of shrimp shell derived electrocatalysts.

References

[1] C. Freire, D. M. Fernandes, M. Nunes, V. K. Abdelkader, ChemCatChem, 10 (2018) 1703-1730.
[2] C. Hu, R. Paul, Q. Dai, L. Dai, Chemical Society Reviews, 50 (2021) 11785–11843.
[3] R. Ramos, V. K. Abdelkader-Fernández, R. Matos, A. F. Peixoto, D. M. Fernandes, Catalysts, 12 (2022) 207.
[4] Y. Ding, S. Huang, Y. Sun, Y. Li, L. Zhu, S. Wang, ChemElectroChem, 8 (2021) 3745.

Acknowledgments

This work was funded by Portuguese funds through Fundação para a Ciência e a Tecnologia (FCT/MCTES) in the framework of the project EXPL/BII-BIO/0436/2021.Thanks are also due to FCT for the projects UIDB/50006/2020 and UIDP/50006/2020. R.M. thanks FCT for the PhD fellowship 2020.05342.BD. I.S.M. thanks FCT for her working contract in the framework of Project EXPL/BII-BIO/0436/2021. D.M.F. and A.F.P. thank FCT for funding through the Individual Call to Scientific Employment Stimulus (Refs. 2021.00771.CEECIND/CP1662/CT0007 and 2020.01614.CEECIND/CP1596/CT0007, respectively). We also thank the company Mar Cabo for providing shrimp shells.

OPTIMIZING CRAB SHELL PROPERTIES FOR ENHANCED CO2 ADSORPTION

Francisco Vicente*, Daniel Pereira, Marina Ilkaeva, Mariana Sardo, Mirtha Lourenço, Ildefonso Marín and Luís Mafra

University of Aveiro, Chemistry Department, CICECO- Aveiro Institute of materials, Aveiro,
seque.vicent@*ua.pt*

Each year approximately 8 million tons of seafood waste is produced and dumped in landfills or the ocean without further treatment.[1] However, given their relevant chemical and physical characteristics (e.g., the presence of chitin, proteins, and natural porosity), these residues may be reused for environmental applications, such as gas capture and separation. In this work, we demonstrate the capabilities of crab shell residues for CO2 adsorption. We implemented mild acid and alkali aqueous treatments to optimize the proportion of chitin, calcium carbonate, and proteins, respectively, increasing its natural porosity towards optimal CO2 adsorption. CO2 adsorption capabilities of the obtained materials were evaluated using several characterization techniques, including gas adsorption isotherms, thermogravimetry, X-ray diffraction, FTIR, and solid-state NMR. Our results show that the untreated crab shell has a CO2 adsorption capacity of 0.18 mmol/g at a pressure of 1 bar and temperature of 298 K. After being subjected to optimized acid/alkali treatments, the resulting material is enhanced in the quantity of chitin and porosity, increasing twice its adsorption capacity. Moreover, the regeneration ability of the optimized adsorbent was tested, performing well under cyclic adsorption-desorption processes. The success of this project will allow the reusing of large quantities of seafood waste to produce an inexpensive and environmental-friendly material for CO2 adsorption.

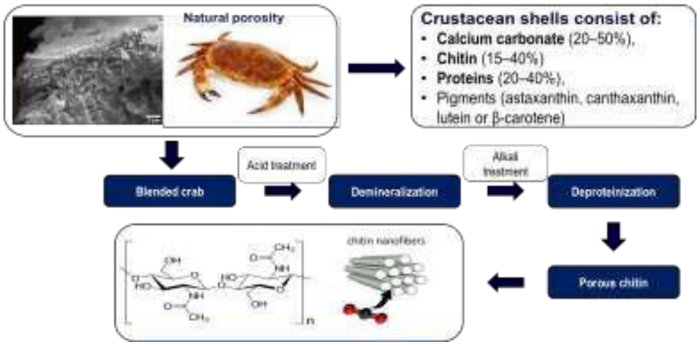


Figure 1. Crab extracted chitin as possible adsorbent for CO2adsorption.

References

[1] J. Smith et al., “Placeholder Text: A Study,” Citation Styles, vol. 3, Jul. 2021.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. We also acknowledge funding from project PTDC/QUI-QFI/28747/2017 (GAS2MAT-DNPSENS - POCI-01-0145-FEDER-028), financed through FCT/MEC and cofinanced by FEDER under the PT2020 Partnership Agreement. The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project 022161 (cofinanced by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). This work has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (Grant Agreement 865974). FCT is also acknowledged by M.I. and M.A.O.L for a Junior Researcher Position (CEECIND/00546/2018 and CEECIND/01158/2021, respectively) and M.S. for an Assistant Research Position (CEECIND/00056/2020). M.A.O.L. further acknowledges the funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement Nº 101090287.

SYNTHESIS AND CHARACTERIZATION OF IRON-BASED METAL-ORGANIC FRAMEWORKS FROM TEREPHTHALIC ACID DERIVATIVES FOR BIOMEDICAL APPLICATIONS

Juliana Araújo,[1,2*] Chrislaura Carmo,[1] Laura C. J. Pereira,[2] Abílio J. F. N. Sobral[1]

[1]Department of Chemistry, University of Coimbra, 3004-535, Coimbra, Portugal; [2]C2TN and Department of Nuclear Sciences and Engineering, Instituto Superior Técnico, Universidade de Lisboa, 2695-066, Bobadela LRS, Portugal.
*juliana.g.araujo2304@gmail.com

Metal-organic frameworks (MOFs) are a type of porous crystalline material constructed by the self-assembly of inorganic metal clusters and organic ligands. These materials have attracted attention over the years due to their unique features including high surface area, high porosity, high crystallinity, open architectures, and biodegradability which enable their applicability in various areas like catalysis, gas storage, selective molecular adsorption, and separation [1]. Moreover, due to the exceptional characteristics of MOFs, they have shown great potential in the biomedical area, more specifically in drug delivery, biosensing, disease diagnosis, and bioimaging. The high porosity and surface area increase the loading of biomolecules and the encapsulations of other particles, the different topologies allow the interaction between biomolecules and the external environment, and biodegradability resulting from the weak coordination bonds is important for the controlled release of drugs [2,3].

In this work, we synthesized Fe-MOFs using the solvothermal method and studied their properties for future application in the biological field [4]. The samples were structurally characterized by means of powder XRD and vibrational spectroscopy and attested the purity and structure of all samples, as shown in the example of MIL-101(Fe) in figure 1. Thermal, microscopic analysis, and magnetic studies of samples were also performed and will be presented.

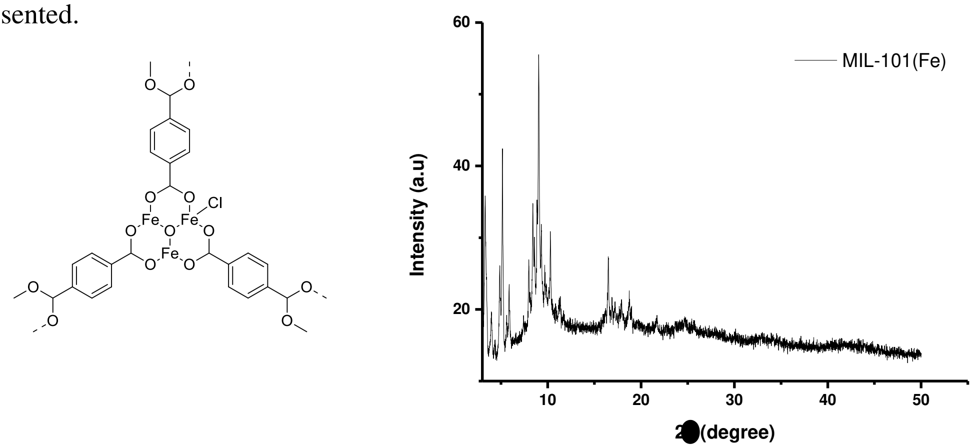


Figure 1: Powder XRD of MIL-101(Fe).

References
[1] M. A. Sharabati, R. Sabouni, G. A. Husseini, Nanomaterials, 12 (2022) 277.
[2] X. Lian, Y. Fang, E. Joseph, Q. Wang, J. Li, S. Banerjee, C. Lollar, X. Wang, H.-C. Zhou, Chem. Soc. Rev., 46 (2017), 3386-3401
[3] H. An, M. Li, J. Gao, Z. Zhang, S. Ma, Y. Chen, Coord. Chem. Rev., 384 (2019), 90-106
[4] A. D. S. Barbosa, D. Julião, D. M. Fernandes, A. F. Peixoto, C. Freire, B. Castro, C. M. Granadeiro, S. S. Balula, L. C. Silva, Polyhedron, 127 (2017), 464-470

Acknowledgments
Thanks to ChemMat PhD program from the Fundação para a Ciência e Tecnologia (FCT, MEC, Portugal) for their general financial support (PD/BD/150440/2019) (SFRH/BPD/103103/2014), and to Centro de Química (UIDB/00313/2020) of University of Coimbra. Authors thank also to C2TN, (UID/Multi/04349/2022, and LISBOA-01-0145-FEDER-022096) (IST, UL) and Trace Analysis and Imaging Laboratory (TAIL-UC) funded under QREN-Mais Centro Project ICT_2009_02_012_1890

P42

INFLUENCE OF REINFORCING FIBER'S PARTICLE SIZE IN PBS-BASED COMPOSITES

Francisco J.P.M.Sousa,[1*] Carolina F.Jesus,[1] Joana R. Góis,[2] Nelson A.M.Pereira,[3] Filipe E.Antunes[1,4]

[1]Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal.
[2]United Biopolymers, S.A, 3090-451 Figueira da Foz, Portugal,
[3]United Resins, S.A, 3090-451 Figueira da Foz, Portuga,
[4]Science 351, Instituo Pedro Nunes, Rua Pedro Nunes C, 3030-199 Coimbra, Portugal.
*fsousa@qui.uc.pt

Global pollution from conventional plastics of petrochemical origin is increasing year by year, causing serious, mostly irreversible environmental damage. In recent years, several scientific projects have focused on the development of new technologies in order to obtain fully biodegradable and/or compostable materials.[1]

Plant fibers used as reinforcement in biodegradable composites make these materials suitable for many industrial and household applications. However, continuous research is needed to find new compatibilization methods that improve the physicochemical properties of the final products. [2] In addition, awareness of a circular economy has gained attention in most industries. [3]

Physical or chemical treatments of cellulosic fibers are one of the most commonly used strategies to improve the interfacial adhesion between hydrophilic fibers and hydrophobic polymers. [4] In this context, this project conducted a comparative study of two different particle sizes of sulfite pulp used as reinforcing fibers (grinding in a blender and grinding in a ball mill), a by-product from the pulp and paper industries, in terms of mechanical performance, water absorption and wettability. The results showed a strong correlation between particle size and the evaluated physicochemical properties.

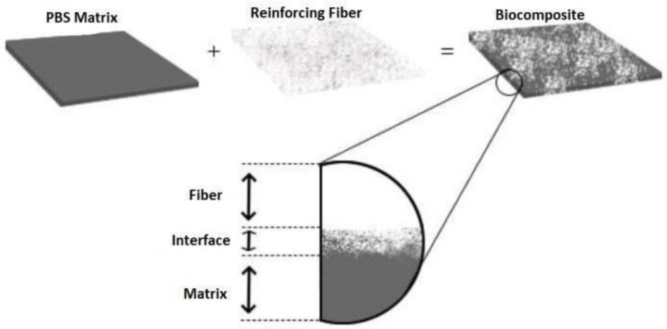


Figure 1: Illustration of a biocomposite structure. [5]

References [List references cited in text as]
[1] Geyer, R.; Jambeck, J. R.; Law, K. L. Sci. Adv. 2017, 3, 1–5.
[2] Sanjay, M. R.; Siengchin, S.; Parameswaranpillai, J.; Jawaid, M.; Pruncu, C. I.; Khan, A. Carbohydr. Polym. 2019, 207, 108 121.
[3] Kumar, R.; Verma, A.; Shome, A.; Sinha, R.; Sinha, S.; Jha, P. K.; Kumar, R.; Kumar, P.; Shubham; Das, S.; Sharma, P.; Prasad, P. V. V. Sustain. 2021, 13, 1–40.
[4] Ahmad, R.; Hamid, R.; Osman, S. A. Adv. Civ. Eng. 2019, 2019.
[5] Khagendra, K.; Yadav, S.; Lohchab, D. *Int. Adv. Res. J. Sci. Eng. Technol.* 2016, *3* (4), 58–65.

Acknowledgments
This work was supported by B2-Solutions project (reference: POCI-01-0247-FEDER-048505), co-financed by ERDF, through the "PT2020 program, within the framework of the SII&DT and COMPETE 2020. The authors also thanks to CELBI

LANTHANIDE DOPED SILICA-BASED FILM AS A SENSOR FOR AMINES VAPOURS DETECTION AND DISCRIMINATION

Cláudio M. R. Almeida[1,2,*], João pina[4], Júlia M. C. S. Magalhães[2], Fátima 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.
[4] University of Coimbra, CQC-IMS, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal.
*claudio@eq.uc.pt

Amines are a class of molecules with major relevance in biology, pharmaceuticals, and industry. They possess unique properties such as basicity, polarity and hydrogen bonding capacity [1]. Among them, biogenic amines which are formed during food spoilage, represent a problem in the food industry, since some of them poses 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]. Optical sensors, essentially those sensors that use the visible region, present several advantages for on-site inspection operations, mainly because they offer information without the need for complex analytical instruments. These sensors offer the possibility to achieve on-site information, employing basic sample preparation protocols and simple instrumentation, when compared to standard methodologies such as chromatography. However, most of optical sensors for amines have poor selectivity and resolution [3].

In this work, we report a paper-supported co-doped Tb^{3+} and Eu^{3+} silica films, as a retiometric sensing platform for the detection and discrimination of several amines vapours. The developed sensor displays different values in the relative emission intensity ratio (I_{Eu}/I_{Tb}) induced by the amine vapours. The observed variations can be used to discriminate amines based either on their photoluminescence properties and also by "naked-eye" observation.

References

[1] JL Klockow, KS Hettie, TE Glass, Fluorescent Sensors for Amines, 2nd ed.; Elsevier, 2017; Vol. 8., 10.1016/B978-0-12-409547-2.12630-7
[2] Li Y, Wang Z, Sun L, Liu L, Xu C, Kuang H., TrAC Trends in Analytical Chemistry. 2019, 10.1016/j.trac.2019.01.012.
[3] CMR Alemida, JMS Magalhães, MFS Barroso, L Durães, Journal of Materials Chemistry C, 2022, DOI: 10.1039/D2TC03143D.

Acknowledgments

Cláudio M.R. Almeida acknowledges the PhD grant SFRH/BD/150790/2020 by Fundação para a Ciência e a Tecnologia (FCT, Portugal) funded by national funds from MCTES (Ministério da Ciência, Tecnologia e Ensino Superior) and, when appropriate, co-funded by the European Commission through the European Social Fund. This work was also supported by the European Regional Development Fund (ERDF), through COMPETE 2020 – Operational Programme for Competitiveness and Internationalization, combined with Portuguese National Funds, through Fundação para a Ciência e Tecnologia, I.P. [POCI-01-0145-FEDER-006910; UID/EQU/00102/2020;NORTE-01-0145-FEDER-31968; PTDC/NAN-MAT/31968/2017, UIDB/50006/2020; UIDP/50006/2020]. The CQC - IMS is supported by the FCT through the projects UIDB/00313/2020 and UIDP/00313/2020.

MIP NANOPARTICLES FOR SPECIFIC RECOGNITION OF BSA

Figueiredo, Rui,[1] Azenha, Manuel,[1] Pereira, Carlos M.,[1] Ribeiro, José A.[1]

[1] *CIQUP/IMS, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal*

The scientific community is currently making efforts to coming up with alternatives to biological antibodies. In this context, molecularly imprinted polymers (MIPs) have the potential to be a highly promising alternative to their biological counterparts, since these synthetic biomimetic materials ("plastic antibodies") are expected to have a high ability to recognize the target analyte, although they have higher stability and much lower production cost [1]. Moreover, over recent years, the preparation of nanoscale imprinted materials, specifically molecularly imprinted polymer nanoparticles (MIP NPs, also known as nanoMIPs), has found many innovative practical applications, including in the biosensing field [2].

This work consists on the synthesis and characterization of nano sized molecularly imprinted polymers (MIP NPs) for the selective recognition of bovine serum albumin (BSA). Two methods were considered, for MIP nanoparticles synthesis, namely by (i) precipitation polymerization [3] and by (ii) solid-phase approach [4]. In order to characterize the MIPs, different techniques were used, such as DLS, for size estimation, zeta potential to evaluate the colloidal stability of NPs and SPR to measure specific molecular interactions in real time and evaluate nanoMIPs performance. Then, the MIP NPs obtained by the different synthesis methods were compared in order to select the most appropriate biomimetic materials for incorporation into optical transduction devices for detection of BSA in environmental samples with high selectivity and sensitivity.

Keywords: molecularly imprinted polymers; nanoparticles; MIPs NPs; nanoMIPs; biosensor; BSA; optical detection.

References

[1] A.M. Mostafa, S.J. Barton, S.P. Wren, J. Barker, TrAC - Trends in Analytical Chemistry. 144 (2021).
[2] J. Wackerlig, R. Schirhagl, Anal Chem. 88 (2016) 250–261.
[3] K. Yoshimatsu, H. Koide, Y. Hoshino, K.J. Shea, Nat Protoc. 10 (2015) 595–604.
[4] F. Canfarotta, A. Poma, A. Guerreiro, S. Piletsky, Nat Protoc. 11 (2016) 443–455.

Acknowledgments

This research had the financial support of FCT (Fundação para a Ciência e Tecnologia) and co-financed by the European Union (FEDER funds) under the Partnership Agreement PT2020, Research Grant Pest-C/QUI/UIDB/00081/2020 (CIQUP) and LA/P/0056/2020 (IMS). J.A. Ribeiro (ref. SFRH/BPD/105395/2014) acknowledge FCT under the QREN e POPH e Advanced Training, subsidized by European Union and national MEC funds. The authors acknowledge the research project MyTag (ref. PTDC/EEI-EEE/4832/2021), funded by FCT, for financial support.

TREATMENT OF OLIVE WASHING WATER BY COAGULATION-FLOCCULATION-DECANTATION AND UV-A/FENTON

A. R. Teixeira,[1*] N. Jorge,[1,2] M. S. Lucas,[1] J.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, Spain. *ritamourateixeira@gmail.com

In olive oil industry, before the extraction process is necessary a preliminary washing of the olives with potable water [1]. This washing generates an effluent named olive washing water (OWW). It is an effluent, characterized by a dark-green colour and high turbidity, which contains organohalogenated contaminants, long-chain fatty acids and recalcitrant phenolic compounds, well known for their phytotoxic effects [1,2]. Significant amounts of OWW are generated, approximately 1m^3 per processed ton of olives [2]. The OWW disposal is becoming an environmental concern and, it is crucial an adequate treatment. The coagulation-flocculation-decantation process (CFD) promote the destabilization of the colloidal particles and their agglomeration in higher settleable flocs. On the other hand, recent technologies as the advanced oxidation processes (AOPs) are efficient in mineralization a wide range of organic compounds, because make use of highly reactive and non-selective radical species, mainly hydroxyl radicals (HO•) [3,4].

The purpose of this work was to optimize and evaluate the operational conditions of (1) UV-A LED/Fenton process and (2) coagulation-flocculation-decantation process (CFD), for the treatment of an olive washing water. Furthermore, the efficiency removal of organic content by the remaining ferrous sulfate was studied as a sequential process (3) photo-Fenton/CFD and (4) CFD/photo-Fenton.

The catalyst/coagulant and the oxidant tested in this work were iron sulfate ($FeSO_4$) and hydrogen peroxide (H_2O_2), respectively. The photo-Fenton process with UV-A radiation achieved higher organic matter degradation at natural pH=4.1, T=25˚C, $[Fe^{2+}]$=3.60 mM and $[H_2O_2]$=116.4 mM (with gradual addition: 38.8/19.4/19.4/19.4/19.4 mM), corresponding to removals of 80.5% of DOC, 93.7% of COD and 71.4% of total polyphenols (TPh), after 120 minutes of reaction. Regarding to CFD process, operating at natural pH, T=25˚C, $[Fe^{2+}]$=3.60 mM, fast mix: 150 rpm for 3 min and slow mix: 20 rpm for 20 min and, 6 h of sedimentation, removed 26.1% of DOC, 29.1% of COD, 7.2% TPh, 87.9% of turbidity and 49.6% of TSS. The catalyst (ferrous sulfate) feasibility to act as a coagulant/flocculant after the photo-Fenton process was studied, being achieved a global removal of 80.8% of DOC, 94.1% of COD, 71.9% of TPh, 98.5% of turbidity and 91.4% of TSS, after 6 h of sedimentation. In addition, the capacity of the coagulant/flocculant remaining of the CFD process act as catalyst in oxidative process was also tested, resulting in a total reduction of 91.0% of DOC, 97.5% of COD, 76.4% of TPh, 95.7% of turbidity and 89.8% of TSS, after the gradual addition of 116.4 mM of H_2O_2 and 120 min of reaction. As a main conclusion, the combined CFD process followed by UV-A/Fenton can be selected has a promising OWW treatment strategy.

References

[1] F. Cerrone, P. Barghini, C. Pesciaroli, M. Fenice, Chemosphere, 84 (2011) 254–259.
[2] P. Maza-Márquez, A. González-Martínez, B. Rodelas, J. González-López, Bioresour. Technol., 238 (2017) 389–398.
[3] S. Shabir, N. Ilyas, M. Saeed, F. Bibi, R.Z. Sayyed, W.H. Almalki, Environ. Res., 216 (2023) 114399.
[4] B.M. Esteves, C.S.D. Rodrigues, F.J. Maldonado-Hódar, L.M. Madeira, J. Environ. Chem. Eng., 7 (2019) 103252.

Acknowledgments

The authors are grateful for the financial support of the Project AgriFood XXI NORTE-01-0145-FEDER-000041 and Fundação para a Ciência e a Tecnologia (FCT) to CQVR (UIDB/00616/2020). Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.

THE EFFECT OF A STRESSFUL STIMULUS IN BEHAVIOURAL, METABOLIC AND BIOCHEMICAL MARKERS IN ZEBRAFISH

Raquel Vieira,[1*] Carlos Venâcio,[1,2] Luís Félix,[1]

[1]Centre for the Research and Technology of Agro-Environmental and Biological Sciences (CITAB), University of Trás-os-Montes and Alto Douro (UTAD), Vila Real, Portugal; [2] Department of Animal Science, School of Agrarian and Veterinary Sciences, University of Trás-os-Montes and Alto Douro (UTAD), Vila Real, Portugal.
*rsfvieira@utad.pt

Common technical procedures in intensive aquaculture can cause stress in fish and disturb their welfare. The use of anaesthetics is increasingly recommended to reduce these undesirable effects, which can have major cost consequences. Tricaine methanesulphonate (MS-222) is a synthetic anaesthetic frequently used in aquaculture and research, although some studies suggest that this molecule may cause further alterations in fish welfare. In this regard, it is essential to identify chemicals with anaesthetic characteristics that are also safe for fish, the environment, and the consumer in order to permit their safe and sustainable application. The zebrafish is a teleost fish that has been utilized as a research model for species that are regularly produced in aquaculture. However, an animal model showing stress-related changes is needed to test anaesthethic effects of different compounds.

The objective was to replicate a stress condition in zebrafish larvae by using a specific stimulus and then evaluate subsequent changes in larval behaviour and metabolic alterations to develop a model for future testing of compounds capable of reducing this stressor. In further experiments, various anaesthetic compounds were used to examine their efficiency in reducing cortisol, lactate, and glucose levels, energy consumption, ATPase activity, biochemical oxidative stress markers and DNA damage, after applying the stressful stimulus to the larvae.

For this, 96 hpf (hours post-fertilization) zebrafish larvae were placed in 50 mL centrifuge tubes with a final volume of 20 mL of E3 medium. The tubes were shaken and vortexed at 250 rpm for 1 minute. The behaviour was then examined for 10 minutes, 1 hour, and 4 hours following the stimulation.

The results demonstrated a time-dependent increase in distance travelled, glucose level, the oxidation of resazurin in animals stimulated over the time and some oxidative stress markers, that data indicating that this stimulation may be used as a stressful event for zebrafish larvae. However, results show a decrease in cortisol level, lactate, and ATPase in stimulated animals. The DNA damage data did not have significant differences over time and at the biochemical level the differences were not significant either. These results raise the possibility that an alternative pathway is activated by the stimulus, which is not seen by glucocorticoids. An alternative is the mineralocorticoid pathway through the action of RAC1.

Thus, it can be said that this model is promising and will be an asset in the subsequent evaluation of the effects of compounds capable of reducing stressful effects in aquatic animals.

Acknowledgments
This work was financially supported byPortuguese funds by FCT/MCTES - Portuguese "Fundação para a Ciência e Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior", under the project UIDB/04033/2020. Raquel Vieira is thankful for her Ph.D. grant (SFRH/BD/144904/2019) and Luís Félix is thankful for his Junior Researcher contract (2021.00458.CEECIND) both financed by FCT/MCTES.

INACTIVATION OF *ASPERGILLUS BRASILIENSIS* SPORES IN WATER USING ADVANCED OXIDATION PROCESSES

Ana Gomes,[1*] Ana Sampaio,[2] José A. Peres,[1] Marco S. Lucas[1]

[1]Chemistry Center of Vila Real (CQVR), Chemistry Department, ECVA, University of Trás-os-Montes and Alto Douro (UTAD), Quinta de Prados, 5001-801, Vila Real, Portugal. *anafgomes@utad.pt [2]CITAB, 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), ECVA-UTAD, Quinta de Prados, 5001-801, Vila Real, Portugal.

In recent years, the occurrence of filamentous fungi in drinking water has been considered an environmental and human health problem. Therefore, it is very important to find an efficient method to control fungi in aquatic environments. The present study aimed to inactivate spores of *A. brasiliensis* using chemical oxidation technologies called Advanced Oxidation Processes. In a first step, the effect of two oxidants (hydrogen peroxide and potassium persulfate), with and without UV radiation, will be assessed in the inactivation of *A. brasiliensis* spores. The results showed that the inactivation of fungal spores of *A. brasiliensis* can be completely achieved by a single addition of $[H_2O_2]$ = 194 mM within 300 minutes or $[H_2O_2]$ = 388 mM within 180 minutes. Afterwards, the combination of H_2O_2 (194 mM and 388 mM) with UV-A showed to be even more promising, since the spores were inactivated faster, reaching a 4 log reduction in 120 and 60 minutes, respectively. In conclusion, hydrogen peroxide ($[H_2O_2]$ = 388 mM) with UV-radiation (365 nm, time = 60 minutes) proved to be highly effective in inactivating fungal spores with a 4 log reduction. The results suggest that hydrogen peroxide combined with UV-A LEDs can be an attractive alternative for water disinfection, but this application needs further research.

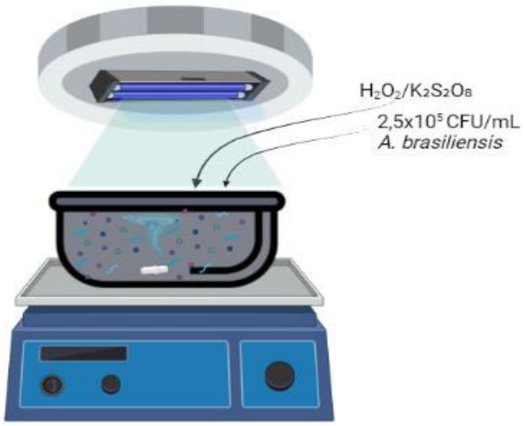


Figure 1: Inactivation of *A. brasiliensis* spores in water by UV-A/H_2O_2 and UV-A/$K_2S_2O_8$.

Acknowledgments

The authors are grateful for the financial support of the project OBTain - Objective Building Sustainability - NORTE-01-0145 FEDER-000084 and Project AgriFood XXI - NORTE-01-0145-FEDER-000041financed by the European Regional Development Fund (FEDER), through the Northern Regional Operational Program. Ana Gomes is grateful for the financial support provided through the OBTain research grant with the reference nº BI/UTAD/67/2022.

ANTIOXIDANT AND MITOCHONDRIAL BIOENERGETIC RESPONSES TO MICROPLASTIC TOXICITY: THE INFLUENCE OF DIET

Mónica G. Silva[1], Mª Manuel Oliveira[1], Francisco Peixoto[1]

[1]CQVR, Centro de Química de Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real
*m.g.27@live.com.pt

Microplastics are currently considered potentially hazardous to human health. What was once one of the top emerging environmental problems is now classified as a one-health issue due to the persistent presence of these particles, resulting in unavoidable human exposure [1]. Indeed, it is recognized by the World Health Organization (WHO) that there is a high probability that these items find their way into humans through several routes [2]. Nonetheless, it is yet to unveil how microplastics may impact human health and how factors such as lifestyle (e.g., diet regimens) influence the toxicological outcomes of these particles. This work aimed to uncover the impact of a high-fat diet in microplastic toxicity on renal mitochondrial bioenergetics and antioxidant function. For that, ICR male mice (5-week-old) were distributed in four experimental groups: STD (animals fed with a standard diet without microplastics); STD+MPs (animals fed with a standard diet without microplastics); HFD (animals fed with a high-fat diet without microplastics); HFD+MPs (animals fed with a high-fat diet with microplastics). Microplastics tested resulted from mechanical degradation of single-use plastics items (e.g., water bottles, plastic bags, straws), with sizes ranging from 90 – 190 nm. A concentration of 0.01% (w/w) of these particles was incorporated in the two diet regimens administered to the animals: standard and high-fat. The high-fat diet was prepared by adding 20 % (v/w) of sugar cane molasses and 10 % (v/w) olive oil to the standard diet.

Serum blood analysis revealed that MPs administered through both diet regimens did not induce kidney damage, as shown by the levels of biomarkers creatinine and urea. However, it led to a significant increase in glucose levels in groups fed with a high-fat diet. Mitochondrial respiratory capacity was evaluated by assessing state 3 and 4 respiratory rates in renal mitochondria energized with complex II substrates (succinate). The oxygen flux remained constant in all experimental groups, showing that neither the microplastics nor the diet impacted the mitochondrial bioenergetics. Administration of microplastics in a standard diet led to oxidative damage, characterized by increased malondialdehyde levels ($p=0.033$), a marker of lipid peroxidation, despite the absence of variation in the protein carbonyl content. An increase in the activity of antioxidant enzymes, such as catalase ($p < 0.0001$), was detected but was not sufficient to prevent oxidative damage produced by the presence of microplastics. Nonetheless, this stimulation maintained cell's redox status, as shown by the constant levels of both reduced and oxidized glutathione. A high-fat diet did not lead to oxidative damage or alterations regarding antioxidant enzymes compared to animals fed with a standard diet. However, it could increase glutathione-S-transferases activity, a phase II biotransformation enzyme. Animals fed a high-fat diet with microplastics showed similar antioxidant responses to those fed the same diet but without microplastics. These findings suggest that different dietary patterns may impact the toxicological effects of microplastic exposure, emphasizing the importance of considering lifestyle factors in toxicological assessments to improve risk analysis regarding microplastics' impacts on human health.

References

[1] J.C. Prata, J.P. da Costa, I. Lopes, A.L. Andrady, A.C. Duarte, T. Rocha-Santos, Science of Total Environment, (2021) 777.
[2] WHO, Microplastics in drinking-water, (2019).

NEW POTENTIAL INSECTICIDE CANDIDATES BASED ON EUGENYL 3-AMINOBENZOATES

José R. A. Coelho,[1*] Renato B. Pereira,[2] David M. Pereira,[2] Elisabete M. S. Castanheira,[3,4] A. Gil Fortes,[1]
Maria José G. Fernandes,[1] M. Sameiro T. Gonçalves[1]

[1]Centre of Chemistry (CQUM), Department of Chemistry, University of Minho, *Campus* de Gualtar, 4710-057 Braga, Portugal;
[2]REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal;
[3]Physics Centre of Minho and Porto Universities (CF-UM-UP), University of Minho, *Campus* de Gualtar, 4710-057 Braga, Portugal;
[4]Associate Laboratory LaPMET, University of Minho, *Campus* de Gualtar, 4710-057 Braga, Portugal.
*a85799@alunos.uminho.pt

The research aimed at the development of new potential pesticides candidates from natural bioactive compounds has currently attracted a great deal of attention. Eugenol, 4-allyl-2-methoxyphenol, the major phenolic compound present in clove essential oil (*Syzygium aromaticum*), display a broad spectrum of biological activities, such as antioxidant, antimicrobial, insecticidal and antifungal [1-3]. It can take part in esterification reactions, through various methods, including by Steglich esterification, a simple and mild reaction that uses 4-dimethylaminopyridine (DMAP) and *N*,*N'*-dicyclohexylcarbodiimide (DCC) [4]. The chemical structure of the used carboxylic acids will be significant in the activity offered by the corresponding esters.

Considering these facts, and as a continuation of our previous work [3,4], 3-aminobenzoic acid and its derivatives having electron donating and electron withdrawing groups were reacted with eugenol by Steglich esterification, in order to evaluate their effect on the biological activity of the respective esters.

The synthesis, full characterization and biological activity against *Sf*9 insect cell lines of the eugenyl 3-aminobenzoates, compared with a commercial synthetic pesticide will be presented.

References

[1] Abdou, A.; Elmakssoudi, A.; El Amrani, A.; Jamal Eddine, J.; Dakir, M., *Med. Chem. Res.* 30 (2021), 1011–1030.
[2] Pinto, E.; Vale-Silva, L.; Cavaleiro, C.; Salgueiro, L., *J. Med. Microbiol.* 58 (2009), 1454–1462.
[3] Fernandes, M.J.G.; Pereira, R.B.; Pereira, D.M.; Fortes, A.G.; Castanheira, E.M.S.; Gonçalves, M.S.T., *Int. J. Mol. Sci.* 21 (2020), 9257.
[4] Coelho, J.R.A.; Vieira, T.F.; Pereira, R.B.; Pereira, D.M.; Castanheira, E.M.S.; Fortes, A.G.; Sousa, S.F.; Fernandes, M.J.G.; Gonçalves, M.S.T., *Chem. Proc.* 12 (2022), 46.

Acknowledgments

We thank the financial support of project PTDC/ASP-AGR/30154/2017 (POCI-01-0145-FEDER-030154) of the COMPETE 2020 program, co-financed by the FEDER and the European Union. The authors acknowledge also to Foundation for Science and Technology (FCT, Portugal), and FEDER-COMPETE-QREN-EU for financial support to the research centres CQ-UM (UID/QUI/00686/2020), CF-UM-UP (UIDB/04650/2020) and REQUIMTE (UIDB/50006/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

POISONOUS MUSHROOMS AS A RENEWABLE FONT FOR GREEN CONDUCTING POLYMERS. A THEORETICAL VIEW

Volodymyr V. Tkach*,[1] José Inácio Ferrão de Paiva Martins [2], Sílvio C. de Oliveira[3], Jarem R. Garcia[4], Viktoriia V. Paientko[5], Petro I. Yagodynets´[1]

[1]Chernivsti National University; 58001, Kotsyubynsky Str. 2, Ukraine [2]Faculdade de Engenharia da Universidade do Porto, 4200-465, Rua Dr. Roberto Frias, s/n, Porto, Portugal, [3] Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil, [4] Universidade Estadual de Ponta Grossa, Campus de Uvaranas, Av. Gal. Carlos Cavalcanti, 4748, 84030-900, Ponta Grossa, PR, Brazil [5]Politechnika Lubelska, 20618, Lublin, Poland
*nightwatcher2401@gmail.com

Conducting polymers are among the most studied classes of materials worldwide. Being capable of combining the properties of plastics with metal conductivity they have a wide number of applications, beginning on the anticorrosive coatings and finishing by sensors and biosensors. Another important property of conducting polymers is their tunability [1].

Generally, the conducting polymers are made by chemical or electrochemical polymerization of synthetic monomers, including carbocyclic (aniline, phenols) and heterocyclic (thiophene, pyrrole, indole) compounds. The dye polymers, used for electroanalysis [2] play a specific role in modern sensor investigation. Nevertheless, some natural compounds may also be used as monomers. Moreover, the use of poisonous plants and mushrooms as a renewable natural font for monomers, which is not included in the human trophic chain, may make the resulting conducting polymer even more sustainable and green.

Some toxic compounds from poisonous mushrooms (Fig. 1) may be considered as potential monomers, like phenols from *A. Xanthodermus* and indolic compound psilocin from *Ps. Cubensis*. Their polymers could substitute the polymers from synthetic thiophenes, pyrroles and anilines being somehow more efficient.

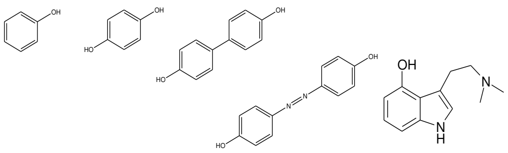


Figure 1: Figure caption [times new roman, 8, plain, centered, line spacing 1.0].

In this work, the possibility for the use of the potential monomers from *A. Xanthodermus* and *Ps. Cubensis* is evaluated from the theoretical point of view. The polymerization is carried on by anodic route, leading to the polymer electrodeposition. The polymer deposition is accompanied by the micromolecular oxidation compound formation, acting as co-dopants.

The analysis of the trivariant mathematicals, correspondent to psilocin and *A. Xanthodermus* polyphenols confirms the efficacy of the electropolymerization process for all of the mentioned compounds. The polymers are to be characterized by high conductivity and electrocatalytic activity in electrochemical sensing.

References
[1] S. Ramanavicius, A. Ramanavicius, Adv. Coll. Interf. Sci., 205(2022), 102693
[2] V.V. Tkach, J.I.F.P. Martins, Ya. G. Ivanushko, P.I. Yagodynets´, Biointerface Res. Appl. Chem., 12(2022), 4028

SYNTHESIS OF SYMMETRICAL AND NON-SYMMETRICAL 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 main method for the synthesis of nitrobenzenes involves the electrophilic aromatic nitration of arenes using a mixture of nitric acid and sulphuric acid, ordinarily known as a “mixed acid” methodology. This type of compounds has been explored in the production of a variety of chemicals, like dyes, perfumes and pharmaceutical products [1]. Recently, new methods for the synthesis of the nitrobenzenes have emerged, such as the direct oxidation of anilines [2] or the *ipso*-nitration of aryl and heteroaryl precursors, allowing the preparation of multiple substituted nitro derivatives [3]. However, these methods imply the application of harsh conditions, raising problems of environmental nature, especially when applied in large-scale production of nitro group-containing compounds, or the use of transition-metals that will lead the production of undesired waste.

Therefore, the search for alternative methods capable of producing these nitrobenzenes using milder conditions are of the upmost importance for both laboratorial and industrial applications. Following the interest in chromones within the research group , we developed a method for the synthesis of nitrobenzenes using 3-formylchromone and nitromethane, as Michael acceptor and donor, respectively, leading to the one-pot formation of three new C–C allowing us to reach the synthesis of 3,5-disubstituted nitrobenzenes over mild conditions. These compounds were obtained in a range of 52-86% isolated yields and the method was found to be compatible with a gram-scale protocol [4]. Following this work, we aimed to further explore this method allowing us to achieve the synthesis of non-symmetrical nitrobenzenes unlocking a whole new range of possible compounds of interest (Figure 1).

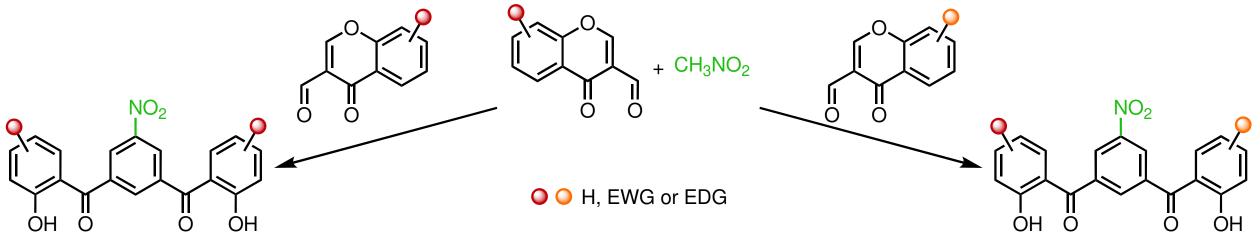


Figure 1: Representation of the synthesis of the desired 3,5-disubstituted nitrobenzenes, symmetrically and non-symmetrically.

References

[1] The Nitro Group in Organic Synthesis. N. Ono, Wiley-VCH 2001.
[2] D. Tanini, C. Dalia, A. Capperucci, Green Chem., 23 (2021) 5680.
[3] C. Wu, Q. Bian, T. Ding, M. Tang, W. Zhang, Y. Xu, B. Liu, H. Xu, H.-B. Li, H. Fu, ACS Catal., 11 (2021) 9561.
[4] T. N. Francisco, J. L. C. Sousa, S. Guieu, A. M. S. Silva, H. M. T. Albuquerque, Synlett, 33 (2022) 1505.

Acknowledgments

This work received financial support from PT national funds (OE) through FCT/MCTES (Fundação para a Ciência e a Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) within the projects: LAQV-REQUIMTE (UIDB/50006/2020 and UIDP/50006/2020), and MuTaTher-AD – “Multi-target theranostics for Alzheimer’s disease” (2022.06064.PTDC). Joana Sousa gratefully acknowledges LAQV-REQUIMTE for her researcher contract. Telmo N. Francisco 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 (2022.12243.BD).

THE INSTABILITY OF Π-BONDS AFTER THE NITRONE'S *O*-ADDITIONS AND [3+2]-CYCLOADDITIONS

Ricardo A. L. S. Santos,[1,2*] Artur M. S. Silva,[1,2] Diana C. G. A. Pinto,[1,2]

[1]LAQV-REQUIMTE, Portugal; [2]Chemistry Department, University of Aveiro, Campus Universitário de Santiago 3810-193 Aveiro, Portugal. *ricardossantos@ua.pt

The nitrones (imine *N*-oxides) are key intermediates in organic synthesis. They are easy to prepare, and the versatility of reaction options is immense. However, to unlock their full potential, one must understand the characteristic reaction behavior of the nitrone functionality.

The most common transformation of nitrones is the [3+2]-cycloaddition to dipolarophiles, which include the addition to alkenes, alkynes, allenes, and others. Whereas the first case forms stable products, the others often rearrange to other structures (**Figure 1**). The reason seems to be the presence of a π-bond in the product, right next to the oxygen. Thus, those unstable intermediates undergo sigmatropic reactions, resulting in α-amino ketones, α,β-unsaturated β-amino ketones and indoles [1,2,3,4,5].

The *O*-additions found in literature also present that structural pattern (the π-bond next to the oxygen). Hence, it is not weird to find heteroatoms at the α-position in the products after another sigmatropy [1,2,6,7]. These reactions compose parts of two sections of a short, comprehensive and updated nitrones' review, to be published soon by the authors.

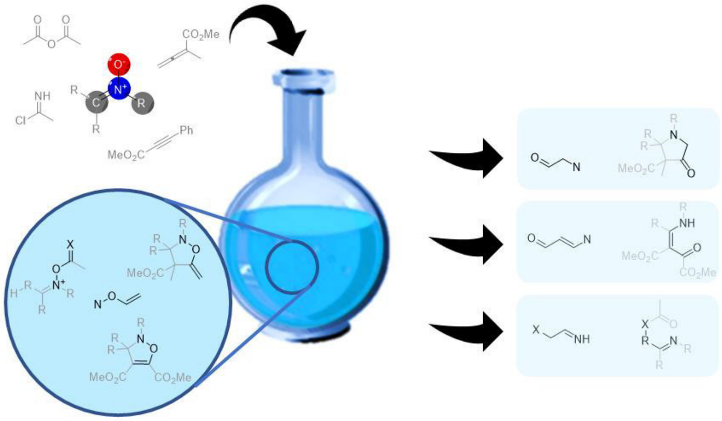


Figure 1: Graphical Abstract – the reagents, intermediates and products of some nitrones *O*-additions and [3+2]-cycloadditions.

References

[1] Nitrile oxides, nitrones and nitronates in organic synthesis: novel strategies in synthesis, H. Feuer (Eds.), Hoboken, John Wiley & Sons, 2008.
[2] S. Murahashi, Y. Imada, Chemical Reviews, 119 (2016) 4684.
[3] L. Anderson, Asian Journal of Organic Chemistry, 5 (2016) 9.
[4] D. Black, R. Crozier, V. Davis, Synthesis, 1975 (1975) 205.
[5] A. Padwa, D. Kline, K. Koehler, M. Matzinger, M. Venkatramanan, The Journal of Organic Chemistry, 52 (1987) 3909.
[6] D. Barton, N. Gutteridge, R. Hesse, M. Pechet, The Journal of Organic Chemistry, 34 (1969) 1473.
[7] I. Santos, W. Zhang, Tetrahedron Letters, 35 (1994) 597.

Acknowledgments

Thanks are due to the University of Aveiro and Portuguese National Funds, through FCT (Fundação para a Ciência e Tecnologia), and as applicable co-financed by FEDER within the PT2020 Partnership agreement by funding the LAQV-REQUIMTE (UIDB/50006/2020). RALS Santos thanks FCT for his PhD grant (UI/BD/151268/2021).

Funding

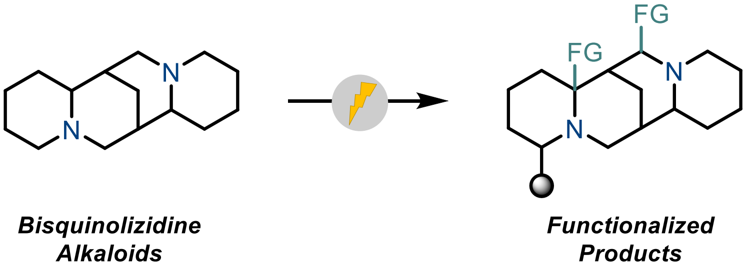
This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

FUNCTIONALIZATION OF NATURAL BISQUINOLIZIDINE ALKALOIDS

Abdullahi A. Muiz,[1] Jaime A.S. Coelho[1]

[1]Centro de Química Estrutural.Institute of Molecular Sciences, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Lisboa 1749-016, Portugal. aamuiz@fc.ul.pt

Bisquinolizidine alkaloids (BQA) are found in several plants of the subfamily *Faboideae*. Structurally, they contain chiral bispidine core decorated with fused N-annulated piperidinone or piperidine moieties [1]. An important member of the group is sparteine, which is commonly used as a chiral ligand for various metals in asymmetric synthesis [2]. However, the limited reactive functional groups on sparteine and other BQA pose a functionalization challenge. Thus, limiting their use in metal-free organocatalysis. Taking advantage of the recent advances in electrochemical organic synthesis that enables gram scale reaction, a site-selective electrochemical C-H activation was explored, and several functional group transformations are currently being investigated (**Scheme 1**) [3].



Scheme 1: Electrochemical functionalization of Bisquinolizidine alkaloids

References

[1] Joseph P. Michael, Simple Indolizidine and Quinolizidine Alkaloids, Hans-Joachim Knölker (Ed), The Alkaloids: Chemistry and Biology, Academic Press, 2016, 75, 1-498**.**

[2] Chuzel O., Riant O., Sparteine as a Chiral Ligand for Asymmetric Catalysis. In: LemaireM., Mangeney P. (eds) Chiral Diazaligands for Asymmetric Synthesis. Topics in Organometallic Chemistry, 2005, vol 15. Springer, Berlin, Heidelberg.

[3] Markus D. Kärkäs, Electrochemical strategies for C–H functionalization and C–N bond formation, Chem. Soc. Rev. 47 (2018) 5786-5865.

Acknowledgments

We thank the FCT for financial support (UIDB/04138/2020, UIDP/04138/2020, UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020 and PTDC/QUI-QOR/1786/2021). JASC thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND.

ELECTROCHEMICAL CYANATION OF SPARTEINE IN CONTINUOUS FLOW

Duarte B. Clemente,[1,2,4*] Sara Lima,[1,3] Carlos A. M. Afonso,[4] Jaime A. S. Coelho[1]

[1]Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa; [2]Departament of Chemistry and Biochemistry, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016, Lisbon, Portugal; [3]Department of Chemistry, NOVA School of Science and Technology, Caparica, 2829-516, Portugal; [4] Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal.
*duarteclemente@alunos.fc.ul.pt

Synthetic organic electrochemistry provides chemists the opportunity to perform highly chemoselective transformations, allowing for high functional group tolerance and mild reaction conditions and being environmentally friendly and scalable [1]. The combination of electrochemistry with flow chemistry increases control over the reaction parameters, enhancing reactivity and improving the reproducibility of electrochemical methods [2,3]. Sparteine is a bisquinolizidine alkaloid that has been widely used as a stoichiometric chiral auxiliary and in asymmetric catalysis, as chiral ligand for lithium, copper and palladium [4]. Herein we report a novel method for the electrochemical cyanation of sparteine in continuous flow. The developed methodology allowed for the functionalization of sparteine, yielding several cyano derivatives that are promising intermediates for the development of unprecedented sparteine-based organocatalysts (**Figure 1**).

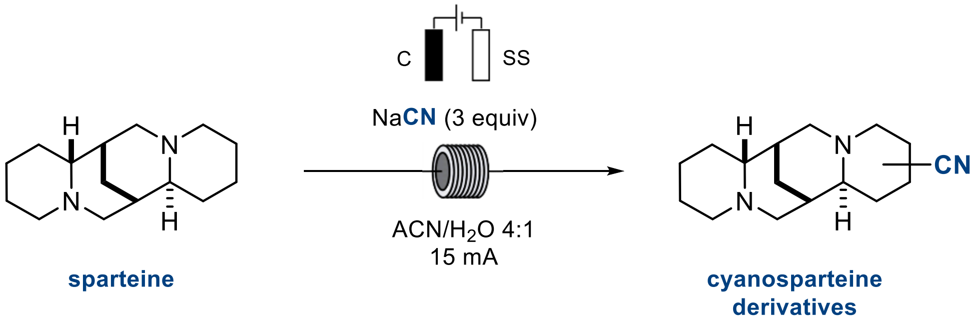


Figure 1: Electrochemical cyanation of sparteine in continuous flow.

References
[1] E. Horn, B. R. Rosen, P. S. Baran, *ACS Cent. Sci.*, 2 (2016), 302.
[2] T. Noël, Y. Cao, G. Laudadio, *Acc. Chem. Res.*, 52 (2019), 2858.
[3] M. Plutschack, B. Pieber, K. Gilmore, P. H. Seeberger, *Chem. Rev.*, 117 (2017), 11796.
[4] Chuzel, O., Riant, O. in: Chiral Diazaligands for Asymmetric Synthesis. Topics in Organometallic Chemistry, M. Lemaire, P. Mangeney (Eds), Springer, Berlin, Heidelberg, 2005, 15.

Acknowledgments

We thank FCT for financial support (UIDB/04138/2020, UIDP/04138/2020, UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020 and PTDC/QUI-QOR/1786/2021). JASC thanks FCT for Scientific Employment Stimulus 2020/02383/CEECIND. The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996.

INCREASING COMPLEXITY OF QUINIC ACID BY PHOTOREDOX CATALYSIS

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] This strategy allowed to increase 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.

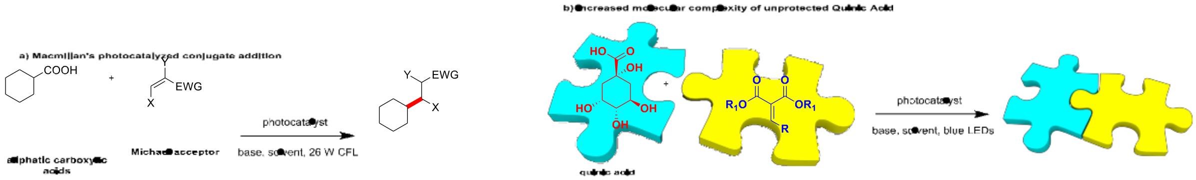


Figure 1. Macmillan's previous work on decarboxylative Michael addition (a). This work (b).

References
[1] Barco, A.; Benetti, S.; Risi, C. D.; Marchetti, P.; Pollini, G. P.; Zanirato, V., Tetrahedron: Asymmetry 1997, 8 (21), 3515-3545.
[2] Holmstedt, S.; George, L.; Koivuporras, A.; Valkonen, A.; Candeias, N. R., Org. Lett. 2020, 22 (21), 8370-8375. [3] Holmstedt, S.; Efimov, A.; Candeias, N. R., Org Lett 2021, 23 (8), 3083-3087.
[4] Huang, C.-Y.; Chen, L.-H.; Huang, H.-Y.; Kao, F.-S.; Lee, Y.-T.; Selvaraju, M.; Sun, C.-M.; Chen, H.-M., RSC Advances 2015, 5 (63), 50801-50806.
[5] Chu, L.; Ohta, C.; Zuo, Z.; MacMillan, D. W., J Am Chem Soc 2014, 136 (31), 10886-9.
[6] Le, C. C.; Wismer, M. K.; Shi, Z. C.; Zhang, R.; Conway, D. V.; Li, G.; Vachal, P.; Davies, I. W.; MacMillan, D. W. C., A, ACS Cent Sci 2017, 3 (6), 647-653.

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. JP thanks FCT for his PhD grant UI/BD/153616/2022.

Funding
This work received financial support from PT national funds (FCT/MCTES) through the projects UIDB/50006/2020, UIDP/50006/2020 and PTDC/QUI-QOR/1131/2020.

SYNTHESIS AND CATALYTIC STUDIES OF IRON TRICARBONYL CYCLOPENTADIENONES ON HYDROGEN BORROWING AMINATION OF CYCLITOLS

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 by cheap and Earth-abundant metals like Fe, Cu, Co or Ni. Iron is a privileged metal from this last set since it is the second most abundant metal on the Earth's crust, is biocompatible, and has a wide range of oxidation states.[1] Iron heterogeneous catalysts are used in the industry to produce syngas and ammonia; however, the development of homogenous iron catalysts has only been explored in the last 15 years, determining a "new iron age". [2][3] A promising class of homogenous iron catalysts are iron tricarbonyl cyclopentadienones (ITCs), 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 various reactions, such as hydrogenation, oxidation and hydrogen borrowing.[5] Herein, we present the synthesis of novel ITCs and their catalytic activity on hydrogen borrowing reactions, targeting the amination of quinic acid and its derivatives (Figure 1).

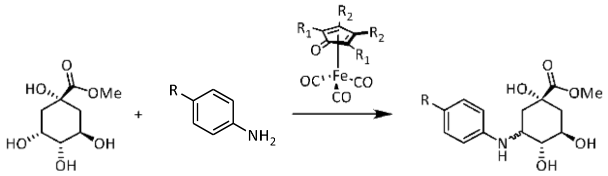


Figure 1: Amination of quinic acid catalyzed by iron tricarbonyl cyclopentadienones.

References
[1] A. Jones, Journal of Catalysis 47 (1977), 384.
[2] F. Moccia, L. Rigamonti, A. Messori, V. Zanotti, R. Mazzoni, Molecules, 26 (2021) 2728.
[3] C. Bolm, Nature Chemistry 1(2009), 420.
[4] Y. Shvo, D. Czarkie, Y. Rahamim, D. F. Chodosh, Journal of the American Chemical Society, 108(1986), 7400.
[5] M. Akter, P. Anbarasan, Chemistry – An Asian Journal, 16 (2021), 1703.
[6] S. Moulin, H. Dentel, A. Pagnoux-Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J. F. Lohier, J. L. Renaud, Chemistry - A European Journal 19 (2013), 17881.

Acknowledgements
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.

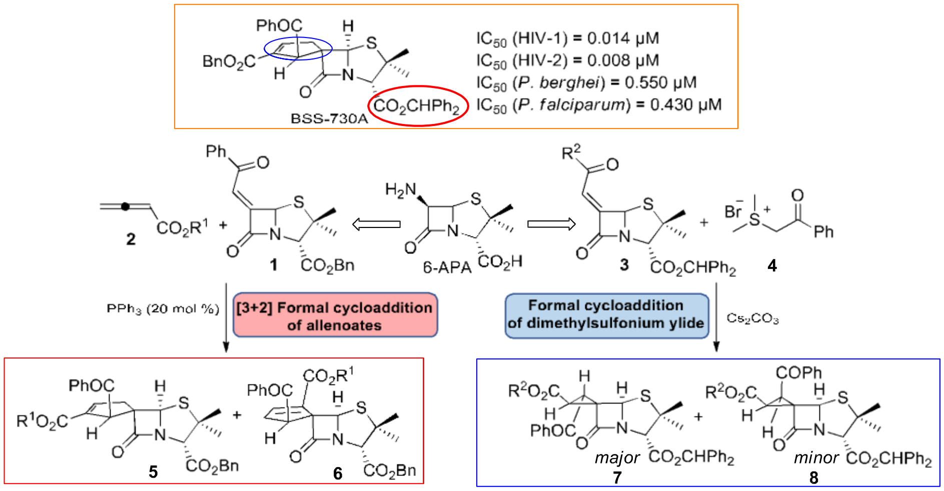
Funding
This work received financial support from PT national funds (FCT/MCTES) through the projects UIDB/50006/2020, UIDP/50006/2020 and PTDC/QUI-QOR/1131/2020.

OVEL SPIRO-PENICILLANATES FROM 6-ALKYLIDENEPENICILLANATES VIA FORMAL CYCLOADDITIONS OF ALLENOATES AND DIMETHYLSULFONIUM YLIDES

João V.R. Gonçalves[1], Américo J.S. Alves[1], Inês Bártolo[2], Nuno Taveira[2], Teresa M.V.D. Pinho e Melo[1]

[1] University of Coimbra, Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS) and Department of Chemistry, 3004-535, Portugal.
[2] Instituto de Investigação do Medicamento (iMed.ULisboa), Lisboa, 1649-003, Portugal.

The β-lactam ring is present in the structure of many biologically active pharmaceuticals, the most iconic being penicillin-G [1]. Recent studies carried out by our group have demonstrated that a family of chiral benzhydryl spiro-penicillanates show a notable sub-micromolar activity against numerous strains of HIV-1 and HIV-2, including multidrug-resistant ones, and against both erythrocytic and hepatic stages of the infection caused by *Plasmodium* [2,3]. These outstanding results motivated the search for novel spiro- penicillanates with improved pharmacokinetics and pharmacodynamics properties. In this context, two distinct structural modulations of the lead compound BSS-730A were explored. The first strategy comprises the synthesis of a novel 6-alkylidenepenicillanate **1**, where the benzhydryl ester of BSS-730A was replaced by a benzyl ester group. Subsequent phosphine-catalyzed [3+2] formal cycloaddition of **1** with allenoates **2** allowed the synthesis of spirocyclopentene-β-lactams **5** and **6**, in up to 48 % overall yield. The second approach relied on the modulation of the spirocyclic ring nature. This goal was achieved via *in situ* generation of a sulfur ylide intermediate, from the correspondent sulfur salt **4** in the presence of Cs2CO3, which readily reacts with benzhydryl 6-alkylidenepenicillanates **3** allowing the synthesis of novel spirocyclopropane-β-lactams **7** and **8** in a diastereoselective fashion in up to 60 % overall yield (**Scheme 1**). Further details of this study will be disclosed.



Scheme 1: Synthesis of novel spiro-penicillanates from 6-alkylidenepenicillanates via formal cycloaddition of allenoates and dimethylsulfonium ylides.

References

[1] Sandanayaka, V. P., Prashad, A. S., Yang, Y., *et al.,* J. Med. Chem., 46 (2003), 2569.
[2] Bártolo, I., Alves, A. J. S., Pinho e Melo, T. M. V. D., *et al.,* ACS Infect. Dis., 7 (2021), 421.
[3] Alves, A. J. S., Alves, N.G., Pinho e Melo, T. M. V. D., *et al.,* Front. Chem, 10 (2022), 1017250.

Acknowledgments

The Coimbra Chemistry Centre-Institute of Molecular Sciences (CQC-IMS) is supported by the Portuguese Agency for Scientific Research, "Fundação para a Ciência e a Tecnologia" (FCT) through projects UIBD/00313/2020 and UIDP/00313/2020 (National Funds) and the IMS special complementary funds provided by FCT. We also acknowledge the UC-NMR facility for producing the NMR data (www.nmrccc.uc.pt).

SYNTHESIS AND STRUCTURAL AND PHOTOPHYSICAL CHARACTERIZATIONS OF DIKETOPYRROLOPYRROLES FOR TECHNICAL AND BIOLOGICAL APPLICATIONS

Vítor A. S. Almodôvar,[1] Augusto C. Tomé[1]

[1]LAQV-Requimte and 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 is attractive for exploring their chemical reactivity towards transformation into derivatives with improved performance or novel application properties [1,3].

This work presents a series of new diketopyrrolopyrrole derivatives synthesized from the cheap commercial Pigment Red 254 (DPP) [4]. The structures of all new compounds were confirmed by several spectroscopic techniques, and their photophysical properties were evaluated.

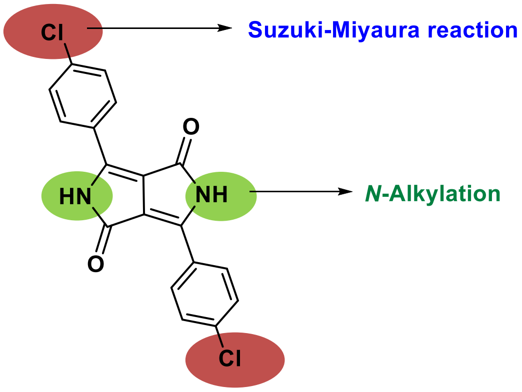


Figure 1. Pigment red 254

References

[1] M. Grzybowski and D. T. Gryko, Adv Opt Mater, 3, (2015), 280.
[2] A. Iqbal, M. Jost, R. Kirchmayr, J. Pfenninger, A. Rochat, O. Wallquist, Bull. Soc. Chim. Belg., 97, (1988), 615.
[3] A. Ruiz-Carretero, N. R. A. Rovelo, S. Militzer, P. J. Mesini, J. Mater. Chem. A, 7, (2019), 23451
[4] V.A.S. Almodôvar, A.C. Tomé, Molecules 26, (2021), 4758.

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) for LAQV-REQUIMTE through the projects UIDB/50006/2020 and UIDP/50006/2020.

Acknowledgements

Thanks are due to the University of Aveiro and FCT/MCTES for the financial support through PT national funds for LAQV-REQUIMTE (UIDB/50006/2020 and UIDP/50006/2020), within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. Vítor A. S. Almodovar thanks FCT/MCTES for her doctoral grant (SFRH/BD/135598/2018)

EFFICIENT DESIGN OF DI-*TERT*-BUTLY-DIPHENYLDIBENZOFULVENE DERIVATIVES WITH ENHANCED AGGREGATION-INDUCED EMISSION

Carla Cunha,[1*] Mariana Peixoto,[1] Joana Santos,[1] Paulo Abreu,[1] Marta Pineiro,[1] J. Sérgio Seixas de Melo[1]

[1]University of Coimbra, CQC, Department of Chemistry, Rua Larga, Coimbra 3004-535, Portugal. *cssddcunha@gmail.com

Aggregation-induced emission (AIE), a phenomena coined by Ben Z. Tang and coworkers in 2001 to explain the high increase in the luminescence efficiency in solution/film of a bad solvent, in comparison with a good solvent, has now reached its level of maturity.[1] In its early days molecules displaying this effect (AIEgens) included the core structures hexaphenylsilole (HPS), tetraphenylethylene (TPE), phenothiazine (PTZ), whereas nowadays it has spanned to many other families of molecules and polymers and, more recently, to diphenyldibenzofulvene derivatives (DPBF).[2] Recently we showed that the *tert*-butyl group has a strong influence in the AIE properties of *tert*-butyl-TPE monomer and polymer structures. In this work, we have, based on a rational design, synthetize and investigate five DPBF derivatives with *tert*-butyl substituents in the fluorene core stator and incremental number of methyl (in the diphenyl moiety rotor) groups. We found that such a wide-range of AIEgens, resulting from the same fluorophore, is rarely reported. Interestingly, the *tert*-butyl substitute has a strong influence on the emissive properties.[3] The characteristics (size and distribution) of the aggregates were further corroborated with dynamic light scattering measurements. From time-resolved fluorescence experiments the increase in the contribution of the longer decay component is found associated to the aggregate emission (AIE effect).[3]

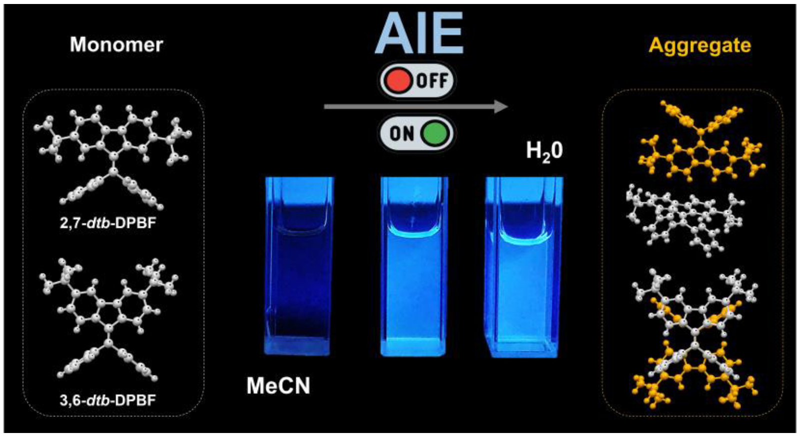


Figure 1: Molecular structure of compound 2,7-*dtb*-DPBF and 3,6-*dtb*-DPBF: monomer (in acetonitrile) and aggregate (in acetonitrile: water mixture, f_w > 60% v/v).

References
[1] J. Luo, Z. Xie, J. W. Y. Lam, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chemical Communications,* 18 (2001), 1740-1741.
[2] Aggregation-Induced Emission. Tang Y, Tang Bz (Eds.), *Springer International Publishing, Cham*, 2022, 209-246.
[3] C. Cunha, M. S. Peixoto, J. Santos, P. E. Abreu, J. A. Paixão, M. Pineiro, J. S. Seixas de Melo, *ACS Appl. Opt. Mater.*, 1 (2023), 1, 340-353.

Acknowledgments
The authors acknowledge funding from FCT, FEDER and Compete Centro 2020 throughout projects Hylight PTDC/QUI-QFI/31625/2017, ROTEIRO/0152/2013, CQC (UIDB/00313/2020 and UIDP/00313/2020) and Laserlab-Europe (no. 284464, EC's 7th Framework Programme). CC gratefully acknowledges FCT by a PhD grant (2020.09661.BD).

SORPTION STUDY OF FURANIC COMPOUNDS IN TRANSFORMERS' INSULATING MATERIALS SYSTEMS

Miguel A. J. Teixeira[1*], Shanika Y. Matharage[2], Zhongdong Wang[2], Mário M. Q. Simões[3], Inês Portugal[1], Carlos M. Silva[1]

[1]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal; [2] Department of Engineering, Centre for Smart Grid, University of Exeter, Exeter, United Kingdom; [3]LAQV- REQUIMTE, Department of Chemistry, University of Aveiro, Aveiro, Portugal. *ma.teixeira@ua.pt

Transformer insulation system is mainly consisted of cellulosic materials and mineral oil. Results from laboratory scale ageing experiments with these insulation materials not only provide information about the degradation processes of these materials but also other information such as the behavior of degradation markers that help for early detection of faulty transformers in-service. Among degradation markers, the presence of furanic compounds (furfural, furfuryl alcohol, 5-hydroxymethylfurfural, 5-methylfurfural, and 2-acetylfuran) in oil is commonly associated with the degradation of cellulosic materials [1-2] and several correlations have been established between degradation and furfural content [1]. In collaboration with EFACEC, and within the project NEXTRA, preliminary ageing tests of two different insulating papers (Kraft paper and thermally upgraded crepe Kraft paper (TUP)) immersed in oil were performed (in closed systems, at 120 °C, with duration up to 7 weeks). Each week, samples were taken out of the oven and conditioned at room temperature for further 168 hours prior to the oil sampling as the sampling temperature and time may affect the distribution of degradation markers, such as furfural partition [3] in oil-paper systems.

Further to validate the procedures for oil sampling and analysis, sorption tests for furanic compounds (furfural (FAL), and furfuryl alcohol (FOL)) were performed at 30 °C, in an orbital shaker (100 rpm), in the presence of "oil + Kraft paper" or "oil + TUP", with initial concentrations of FAL and FOL, in the oil, in the range from 1 to 100 mg/kg. These samples were conditioned for 168 h (1 week) after which the oil was separated from the paper and analysed by high-performance liquid chromatography (HPLC) with diode-array detection (DAD) and the concentration in the paper was calculated by mass balance. The results indicated that furanic compounds exhibit different sorption kinetics and distribution in the oil-paper systems, with higher affinity for FOL (for both papers) in the studied conditions. Overall, this research contributes to the knowledge of the insulation ageing process and equilibrium and partition of chemical markers within insulation systems.

References

[1] L. Cheim, D. Platts, T. Prevost, S. Xu, IEEE Electr. Insul. Mag., 27 (2011) 29 – 42.
[2] J. Scheirs, G. Camino, M. Avidano, W. Tumiatti, J. Appl. Polym. Sci., 69 (1998) 2541–2547.
[3] L. Yang, Y. Lin, R. Liao, X. Zhao, W. Sun, Y. Zhang, IEEE Trans. Dielectr. Electr. Insul., 23 (2016) 1393–1401.

Acknowledgments

This work is financed by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of Operational Competitiveness and Internationalization Programme (POCI) in the scope of the projects number 39906 NEXTRA- Enabling the NEXT Generation of Smarter TRAnsformers, (POCI -01-0247-FEDER-039906). This work is also in 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/MEC (PIDDAC). The work developed with LAQV 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. Miguel Teixeira thanks FCT for a PhD grant (UI/BD/151139/2021).

ESSENTIAL OILS AND THEIR EMULSIONS: GATHERING ANTIBACTERIAL ACTIVITY AND MOLECULAR DYNAMICS IN UNVEILING NEW ANTISEPTIC COSMETICS

Nélia C. T. Tavares[1*], Diana Monteiro[2], Ulisses F. Marques[1], Carolina F. Jesus[1], Andreia A. S. Alves[3], Hugo A. L. Filipe[1,4], Filipe E. Antunes[1]

[1]CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal; [2]Faculty of Pharmacy, University of Coimbra, 3000-548 Coimbra, Portugal; [3]Science351, Instituto Pedro Nunes, Rua Pedro Nunes C, 3030-199 Coimbra, Portugal; [4]CPIRN-IPG-Center of Potential and Innovation of Natural Resources, Polytechnic Institute of Guarda, 6300-559 Guarda, Portugal. *neliatadeu@hotmail.com

In recent years, one could notice a great change in environmental and ecological awareness. With the growing interest in a healthier lifestyle that puts less strain on the planet and public health, people have drastically changed their routines and personal care habits [1]. This is also reflected in the cosmetics industry, as marketing trends are moving towards natural solutions instead of the most common synthetic ones [2]. The changes are so evident that the natural cosmetics market is expected to grow by $19.6 billion by 2031.

In an effort to develop all-natural cosmetic formulations endowed with antibacterial properties against acne and antimicrobial effects, emulsions based on essential oils have been produced. The antibacterial activity of essential oils (EO) is widely recognized in the literature, where these substrates combine a wide range of other cosmetically beneficial properties, such as antioxidant, anti-inflammatory and aromatic [3,4]. In this work, the effect of EO on gram-positive and -negative bacteria was studied. The higher antibacterial activity (MIC values up to 0.125%) of oregano, thyme and mint EO led to promote their emulsification as a basis for the proposed cosmetic formulations. The effect of the molecular structure of the surfactant was studied in the formation of EO-based emulsions. Under optimized conditions and by adding xanthan gum or carboxymethyl cellulose, emulsions with higher emulsification indices and stabilities were obtained. The antibacterial activity of the polymer-based EO emulsions was determined, significantly lowering the MIC values. A synergistic effect of combinations of EO was also verified. Molecular dynamics simulations made it possible to capture the membrane-disrupting effects of the main molecules of the selected EO, thus rationalizing the experimental results.

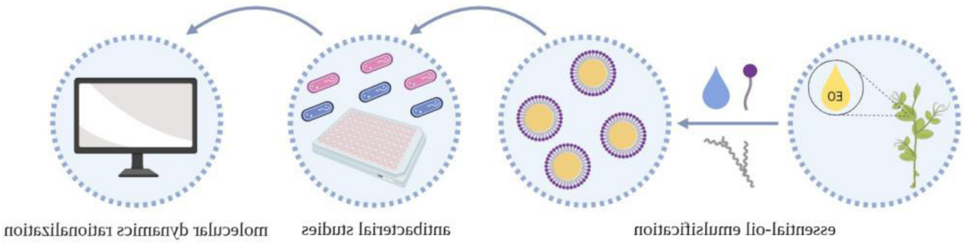


Figure 1

References
[1] C. Barros, R. B. G. Barros, J. Cosmetol. Trichology, 6 (2020)
[2] N. Amberg, C. Fogarassy, Resour., 8 (2019) 137
[3] E. Guzmán, A. Lucia, Cosmetics, 8 (2021) 114
[4] J. B. Sharmeen, F. M. Mahomoodally, G. Zengin, F. Maggi, Molecules, 26 (2021) 666

Acknowledgments
The authors are thankful to PT2020 for financing (project TEAM-ALL CENTRO-01-0247-FEDER-72599). Thanks are due to Coimbra Chemistry Centre, Institute of Molecular Sciences (CQC-IMS), supported by the Portuguese Agency for Scientific Research, FCT.