PROCEEDINGS

of the

Green Chemistry Postgraduate Summer School (online/in-person),

4-9 July 2021, Venice, Italy

Green Sciences For Sustainable Development Foundation

COLLECTION OF ABSTRACTS

Editors: Pietro Tundo, Fabio Aricò, Aurelia Visa and Mirabbos Hojamberdiev

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4-9 JULY, 2021 – ONLINE/IN-PERSON

GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Ca' Foscari University of Venice
Department of Environmental Sciences, Informatics and Statistics

Organizzazione delle Nazioni Unite per l'Educazione, la Scienza e la Cultura
Con il patrocinio della
Commissione Nazionale Italiana per l'UNESCO

GREEN CHEMISTRY *LIVE AND ONLINE* POSTGRADUATE SUMMER SCHOOL

4th-9th July 2021
Venice, Italy

Organizers:
Pietro Tundo Chairman
Fabio Aricò
Aurelia Visa
Mirabbos Hojamberdiev
Elena Alfine
Emilia Pasta

Topics:
Benign synthesis routes
Green catalysis
Alternative solvents
Renewable and green raw materials
Green chemistry for energy
Clean processes
Green Chemistry education

Info at: **https://www.gssd-foundation.org**
www.greenchemistry.school/

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European Chemical Society

Green Chemistry

Airi
ASSOCIAZIONE ITALIANA PER LA RICERCA INDUSTRIALE

twas
THE WORLD ACADEMY OF SCIENCES

The Editors would like to thank Elena Alfine and Emilia Pasta for their wonderful support in the creation of this book.

PROCEEDINGS of the
Green Chemistry Postgraduate
Summer School (online/in-person),
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Organized by

GREEN SCIENCES
FOR SUSTAINABLE
DEVELOPMENT
FOUNDATION

In collaboration with

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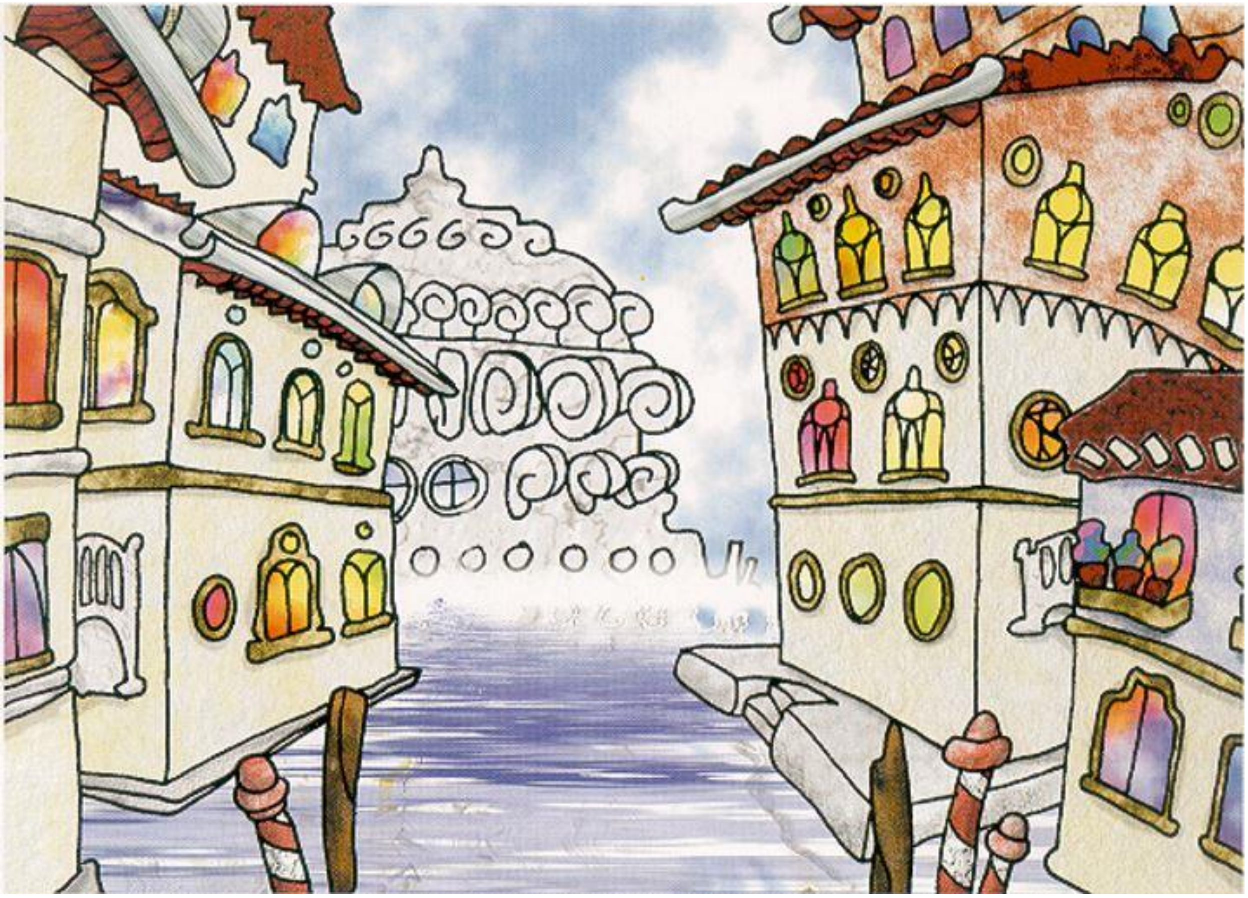
The Summer School was an international initiative organized and managed by the new-born ***Green Sciences for Sustainable Development (GSSD) Foundation*** *(www.gssd-foundation.org), a no-profit Foundation established in February 2020 and based in Venice.*



The Foundation was constituted, pursuant to Article 14 and following of the Italian Civil Code, on February 17th, 2020.

The Foundation has legal personality since it was registered at the Prefecture of Venice on May 28th, 2020 as a non-profit organization. Any proceeds, annuities and profits deriving from the performance of the activities are used exclusively to pursue the purposes of the Foundation.

The Foundation is based in the Municipality of Venice. In order to pursue the statutory purposes, with the resolution of the Board of Directors, secondary offices, agencies and branches may also be established, also abroad.

The Foundation facilitates the participation in its activity of public bodies and administrations and private subjects, developing and increasing the necessary network of national and international relations functional to achieving its goals.

PURPOSES

Main aims of the Foundation are:

a) to encourage the development of scientific education and the dissemination of knowledge in the national and international fields of the sciences of a chemical, physical and environmental order and of the disciplines that care and promote sustainability with particular regard to Sustainable and Green Chemistry and their applications;

b) to support and disseminate scientific, technological and cultural development in Sustainable Development in accordance with the 17 Goals of the United Nations, in the sectors of the use of renewable resources, energy saving, intrinsically clean processes and products, with low or no environmental impact, not harmful to health and green remedies for climate change;

c) to promote initiatives supporting the transfer of research results, the protection of intellectual property and the birth of new entrepreneurship;

d) to promote the involvement and collaboration of public or private, local, national, EU, foreign or international subjects in pursuing the aims of the Foundation itself;

e) to promote the internationalization of teaching and research activities through the management of specific services and participation in joint initiatives with other subjects, public or private, national, EU or international.

ACTIVITIES

a) to organize and manage national and international Congresses and Conferences, education, specialization and updating courses and other advanced training activities such as Summer Schools, Forums and International Thematic Workshops, also in collaboration with other private and public institutions; the sub-Saharan African continent will be paid particular attention;

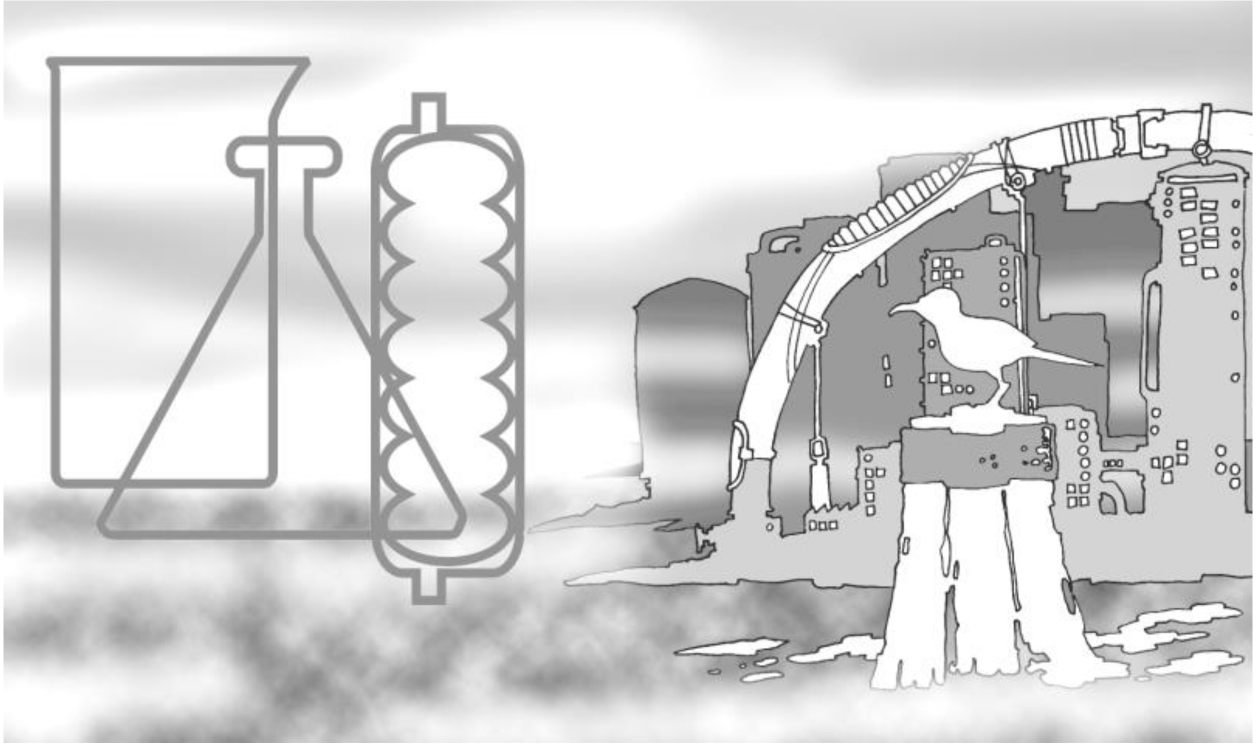
b) to publish books and magazines with their own ISBN;

c) to create and manage any laboratories or research centers also together with other public or private entities;

d) to participate in the operational management of scientific and/or technological structures of other foundations, structures and research bodies;

e) to enter into agreements, contracts, agreements or understandings with other subjects, public or private;

f) to promote and organize the collection of private and public funds and the request for local, national, European and international public and private contributions to be used for the purposes of the Foundation.



GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL
4TH-10TH JULY 2021, ONLINE/IN-PERSON

BOOK OF ABSTRACTS

CONTENTS

WELCOME MESSAGE FROM THE CHAIR OF THE SUMMER SCHOOL

Dear Ladies, Gentlemen, Students, Friends and Colleagues,

I am Pietro Tundo, Chair of the Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation.

It is with great pleasure that I welcome you to the Green Chemistry Postgraduate Summer School which for the first time is held online and onsite; the Summer School has the scientific support of IUPAC, and it is organized by the Green Sciences for Sustainable Development, a non-profit Foundation, with the contribution of Ca’ Foscari University of Venice.

It is a great achievement that about half of the postgraduate students attending the School come from developing countries and have been awarded with a scholarship. So many grants were possible thanks to the Sponsors who believed in our challenge and opportunities: over all the Organization for the Prohibition of Chemical Weapons and PhosAgro. Moreover, this Summer School has obtained the endorsement from UNESCO Roma, from Ministero della Transizione Ecologica, from Veneto Region and from the Municipality of Venice.

This year’s Summer School is more challenging than ever: we wanted to have a school that can be joined in person and online for those who cannot come to Venice yet.

We believe that the present and future participation of Students to the Summer School activities is secured by the top-level scientists and by involving the students in the discussion of the lectures (13 scientific sessions) and, not less important, through the poster sessions, 6 online and 2 in person.

So, the programme is very rich and intensive, and we hope to meet expectations of such many students.

We have a Covid-19 session, in order to better understand what we faced lately, a focus on the climate change and one on energy. Jean-Marie Lehn will give a well-rounded lecture on the future and developments of Chemistry.

Green Chemistry was introduced in 1996; meanwhile Green Chemistry has been evolved. While originally focused on mass-balance, energy saving and non-toxic synthesis, the term is now used in a wider sense, including environmental degradability, recyclability, exploitation of natural resources.

At present, various governments see Green Chemistry as a tool for realising their particular sustainability needs. This is the green agreement. However, different Countries have different problems to solve, of course; thus, we experience now that decision-makers have high expectations for the science of chemistry. This is an emergent, positive and unexpected result, given by globalization. Green Chemistry might be seen as the field in Chemistry which directly responds to the appeal of humankind.

Green Chemistry is a future-oriented approach to reconcile and foster the research in the chemical sciences with society and its needs. So, we necessitate as many as possible new and surprising proposals coming from pure and applied research, in order to have the possibility to select the best solution.

Because most items of modern life are dependent or connected with chemistry, the scientific contribution of Green Chemistry will be essential for global SD.

In conclusion, basic sciences are needed now more than before, as they are the pillars for a sustainable growth.

While we pay attention to the increasing emission of CO_2 and the increasing number of new chemical compounds that are spreading in the environment, it is difficult to foresee an end to this sinister and destructive trend. Nature is not in a hurry but humankind is: we must keep in high consideration the consequences of our rapid industrial development.

A new partnership is necessary among academic, governmental and industrial researchers, to share scientific bases and to cooperate in the management of sustainable development issues.

We may propose that a small portion of profits from industrial activities be reinvested in the sustainable development to be beneficial to everybody. A few industries have already indicated that it is possible to invest up to 5% of their revenues in research and collaboration with Academia in Green Chemistry and sustainable development. This figure might be reasonable given that chemical industry increases constantly and very considerably its business, year after year.

Because of COVID 19, sustainable green growth is said every day to becoming a crucial topic. Is this true? The answer is left to politicians, and we look forward to their feedback.

The experience from the 12 Summer Schools on Green Chemistry, held from 1998-2020 with more than 1000 students attending, tells us that young people are particularly attracted by Green Chemistry, because they look at it as a means to invest their talent at a particular, strategic moment of their lives. Green Chemistry is a good key for students to look around the scientific disciplines and to decide how and where to go forward.

Just to say that five of the 34 teachers of the Summer School were students of one of the previous 12 editions held in Venice. I would like to wish to all students of this edition a great success in their professional careers, with the hope that they will bring back to their Countries remarkable scientific results, as many students from previous editions did.

From the outcomes of this hybrid Summer School we will learn on how to manage the future Schools in Venice, which will become permanent; the Green Sciences for Sustainable Development Foundation will surely support and follow the activities of this initiative.

Our goal is to make the Summer School a permanent event, to be held every Summer in Venice, and thanks to the involvement and the participation of outstanding teachers and partners we are making this objective real.

UN ask us to provide solutions to the needs of the humankind thorough the17 SDGs. Chemistry always was addressed to the exploitation of human and natural resources. Now we can do it much more that in the past. We have to pursue this route decidedly and convinced, without perplexity and, I am sure, we will find many and unexpected chances to invest our intellect.

Alongside the traditional sessions dedicated to Green Chemistry (clean industrial processes and products, new reaction mechanisms, recycling, education), this year a particular relevance will be dedicated to the production of energy (bio and photovoltaic), hydrogen in metallurgy, climate change and the Covid-19 pandemic.

Pietro Tundo
Chair of the Summer School

FOREWORD BY THE HEAD OF CA' FOSCARI DAIS

As the Head of Dept. of Environmental Science, Informatics and Statistics (DAIS) of Ca' Foscari University of Venice, it is a great pleasure for me to welcome you all to this year Green Chemistry Postgraduate Summer School, which will be held in Venice, also online, from July 4 to 9.

I would like to extend the greetings and the wish of good work of the rector of Ca' Foscari, Prof. Tiziana Lippiello (the first female rector of Ca' Foscari), who unfortunately is not able to be present.

According to the CENSIS 2020 survey on Italian universities, the University of Venice is Ca 'Foscari is first in Italy - among medium-sized universities - for internationalization, one of the key points of its Strategic Plan. This achievement is the result of our effort in welcoming international students involved in our programs, in the extended international student/professor exchange programs, in increasing the number of international researchers recruited. Regarding the latest point I would like to mention the numerous Marie Curie fellows and ERC (European Research Council) funding professors.

The research interests of the Department (DAIS) I manage intersect with the ecological transition, which will play a paramount role in the process of the future sustainable development, also thanks to the new research results of Green Chemistry.

Regarding sustainable development, the Veneto Regional Council has recently approved a resolution promoting the development of a project entitled “Venice, the world capital of sustainability”. It is a plan of action “aimed at sustainable development of the area, with the main city in the center”. This initiative is strongly supported by Ca' Foscari University of Venice, Municipality of Venice, the second University of Venice, many industrial companies based in the Venetian Region and other cultural bodies of Venice.

I just want to conclude by underlining once again that Ca’ Foscari, very committed to the international dimension, strongly encourages and sponsors the organization of high-profile international scientific events, such as conferences, schools, meetings, etc, involving its own faculty and researchers. Thus, international well-established events such as the Green Chemistry School, concerning several key-points of the sustainable development and ecological transitions, are, and will always be, very welcome.

Salvatore Orlando
Head of DAIS,
Dept. of Environmental Sciences,
Informatics and Statistics,
Ca' Foscari University of Venice

FOREWORD BY THE PRESIDENT OF IUPAC

It is a pleasure to welcome you all to the Green Chemistry Postgraduate Summer School in 2021 on behalf of IUPAC, the International Union of Pure and Applied Chemistry. IUPAC has had the pleasure and privilege to sponsor the Green Chemistry Summer Schools since the first one in 1997. Last year's Summer School in 2020 took place completely on-line owing to the consequences of the Covid-19 pandemic. Before that the summer school was in Tanzania in 2019 and in-person in Venice in 2018. This year the situation is a little better than in 2020, with some travel being possible, so that the Summer School is a hybrid of in-person and virtual participation. Such hybrid meetings are likely to remain with us, even after the pandemic has passed, since it has become clear that there are significant opportunities available for those potential participants who are unable to travel but are able to participate, learn and contribute on-line. There is a special connection with the Summer Schools through the IUPAC Interdivisional Committee on Green Chemistry for Sustainable Development, ICGCSD, of which Professor Pietro Tundo is chair.

We are all seeking to adjust our lives to the changes caused by the Covid pandemic and are preparing for the post-Covid world, continuing addressing the sustainable development goals.

This summer school and its programme show that green chemistry has implications not just for chemical industry and energy conservation but also on many other aspects of our lives. Our way of life depends on products from chemical industry, on materials and on energy resources. Participants will learn not only about fundamental, basic science and deepen their understanding of their own research area, but will also gain a much wider vision of the most important and latest advances linked to green chemistry and sustainable development. The clock is ticking and we must learn from a renewed awareness of how humankind is affecting the environment and we must learn quickly how to do things better; there is only one planet.

The lectures by world experts on green chemistry and related areas, the questions and answers and the in-person and on-line poster sessions all ensure that the summer school will be a very rewarding experience for teachers and students alike. Professor Pietro Tundo and his team deserve the utmost thanks for organising this hybrid in-person and on-line summer school in what continue to be challenging circumstances. It should lead to new ideas, new contacts, future interactions and collaborations in green and sustainable chemistry; the future depends on us all but particularly on the younger of you. I wish you all an excellent and successful Summer School.

Christopher Brett
IUPAC President

FOREWORD BY THE LOCAL ORGANIZING COMMITTEE IN VENICE

Dear students and teachers of the Green Chemistry Postgraduate Summer School 2021,

It is an honour for me to welcome you to this 13th edition of the school, which is once again held in the wonderful setting of Venice, that has been, and it is still nowadays a crossroads of peoples and cultures.

This is my seventh Summer School, my fourth one as part of the Organizing committee representing Ca' Foscari University. I still vividly remember my first participation at the Summer School. It happened after returning from my experience abroad in America as post-doctoral fellow, when I was invited by Prof Tundo - then director of the Interuniversity Consortium "Chemistry for the Environment (INCA) and creator of the event - to take part to the 2005 edition of the School held in San Servolo, a small island in the Venetian Lagoon. I remember the high quality of the teachers' presentations, the exciting of the young students and the constant buzz of questions, laughter, and conversations about Green Chemistry. Most of the 2005 Summer School students are now grown-up scientists, teachers, professors that still happily remember the School as an amazing opportunity to broaden their knowledges and create new collaborations and friendship for what has then become their future careers. More than 15 years later and despite the recent pandemic outburst I still recognize in the students eyes the same excitement and the desire to explore issues related to Green Chemistry and sustainability nowadays even more intertwined with the world social and economic growth.

The 2021 edition of the Green Chemistry Postgraduate Summer school is most probably the most demanding and the one we are more proud of. Organizing an on-site and on-line event was extremely challenging; in addition to guaranteeing the high-quality of the teachers, the logistics related to the event required an extra effort that we faced with awareness and hopefully brought to fruition.

This year topics range from benign synthetic routes to green catalysts, alternative solvents, renewable and green materials, green energy and green chemistry education. These topics have been selected as they encompass actual, new or emerging issues related to a green and sustainable development of the society and the scientific community.

As in every edition of the Summer School, each student had to present a scientific poster highlighting his actual research topic and interest. The number (almost 100!) and the high-quality of this year poster presentations have been overwhelming and I cannot wait to see how this young scientist will evolve in the future generation of scientific expert that will guide the world toward a greener future.

Fabio Aricò
Professor of Organic Chemistry Ca' Foscari University,
Organizing Committee of the
Green Chemistry Postgraduate Summer School 2021

SUMMER SCHOOL COMMITTEES

CHAIR OF THE SUMMER SCHOOL

- **Pietro Tundo,** *Chair of Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation, Venice, Italy*

LOCAL ORGANIZING COMMITTEE

- **Fabio Aricò,** *Associated professor of Organic Chemistry, Ca' Foscari University of Venice, Italy*
- **Aurelia Visa,** *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*
- **Mirabbos Hojamberdiev,** *Uzbekistan-Japan Innovation Center of Youth, Uzbekistan*
  Technische Universität Berlin, Germany
- **Elena Alfine,** *Green Sciences for Sustainable Development Foundation, Italy*
- **Emilia G. Pasta,** *Green Sciences for Sustainable Development Foundation, Italy*

ZOOM MANAGER

- **Paula de Waal,** *Mentat di De Waal P., Italy*

INTERNATIONAL SCIENTIFIC COMMITTEE (FROM IUPAC - ICGCSD)

- **Florent Allais,** *Directeur de l'URD Agro-Biotechnologies Industrielles (ABI) AgroParisTech, France – Associate member of IUPAC ICGCSD*
- **Fabio Aricò,** *Ca' Foscari University of Venice, Italy*
- **Neil Coville,** *University of the Witwatersrand, Johannesburg, South Africa*
- **Jonathan Forman,** *Science and Technology Advisor in the Global Security Technology and Policy Group under the National Security Directorate of Pacific Northwest National (PNNL), USA – Titular member of IUPAC ICGCSD*
- **Mirabbos Hojamberdiev,** *Uzbekistan-Japan Innovation Center of Youth, Uzbekistan*
  Technische Universität Berlin, Germany
- **Konstantinos S. Triantafyllidis,** *Aristotle University of Thessaloniki, Greece*
- **Pietro Tundo,** *President of the Green Sciences for Sustainable Development Foundation and Ca' Foscari University of Venice, Italy – Chair of IUPAC ICGCSD*
- **Aurelia Visa, Romanian Academy,** *"Coriolan Drăgulescu" Institute of Chemistry, Timisoara, Romania – Associate member of IUPAC ICGCSD*
- **Jane Wissinger,** *Environmental & Green Chemistry, Department of Chemistry, University of Minnesota, USA – Associate member of IUPAC ICGCSD*

INTERNATIONAL JURY FOR THE POSTER SESSIONS

- **Neil Coville**, *Chairman of the Jury and Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*
- **Pietro Tundo,** *Chair of Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation, Venice, Italy*
- **Aurelia Visa**, *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*

- **Mirabbos Hojamberdiev,** *Uzbekistan-Japan Innovation Center of Youth, Uzbekistan*
  Technische Universität Berlin, Germany
- **Fabio Aricò,** *Associated professor of Organic Chemistry, Ca' Foscari University of Venice, Italy*

PLENARY LECTURES

JEAN-MARIE LEHN
ISIS, Université de Strasbourg, France
Perspectives in Chemistry: Molecular – Supramolecular – Adaptive Chemistry

PIETRO R. TUNDO
Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University, Venezia, and *President of Green Sciences for Sustainable Development Foundation, Venice*
Reaction Mechanisms and Energy Profiles: How Green Chemistry Complies With Them. The Case of Dimethyl Carbonate.

MICHAEL GRAETZEL
Laboratory of Photonics and Interfaces, Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland
Mesoscopic Photosystems for the Generation of Electricity and Fuels From Sunlight

ALESSANDRO MARTINIS
Vice President, Danieli Centro Metallics, Italy
Low Carbon Emission Green Steelmaking is Possible

CARLO BARBANTE
Institute of Polar Sciences and Ca' Foscari University of Venice
Too late for 2°C? From the Paris Agreement to the Climate of Tomorrow

KRZYSZTOF MATYJASZEWSKI
Carnegie Mellon University, Center for Macromolecular Engineering, Pittsburgh, PA, 15213, USA
Green Materials by Atom Transfer Radical Polymerization under Benign Conditions

Burkhard KÖNIG
Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany
Using Visible Light For More Sustainable Organic Synthesis

LECTURES & TEACHERS
(alphabetical order)

FLORENT ALLAIS
Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France
Biomass Upgrading Through the Combination of Biotechnology, Green Chemistry & Downstream Process

PAUL T. ANASTAS
Director of Photonics and Interfaces (LPI), Institute of Chemical Science and Engineering Faculty of Basic Science Ecole Polytechnique Federale de Lausanne, Switzerland
The Periodic Table of the Elements of Green and Sustainable Chemistry

FABIO ARICÒ
Ca' Foscari University, Campus Scientifico, via Torino 155, 30172 Venezia (IT)
Bio-based Platform Chemicals and Dialkyl Carbonates: A Green Match

EMILIANO CAZZOLA
IRCCS Sacro Cuore Hospital, Cyclotron & Radiopharmacy Dept, via Sempreboni 5, Negrar (Vr), Italy
Green Radiochemistry: Dream or Reality?

JAMES CLARK
Professor of Chemistry at the University of York; Founding Director of the Green Chemistry Centre of Excellence and the Bio-renewables Development Centre, United Kingdom
Bio-Based Solvents and Their Selection

JONATHAN E. FORMAN
Science and Technology Advisor, Global Security Technology and Policy, Pacific Northwest National Laboratory, Seattle, WA 98109 USA
Chemical Disarmament, Non-Proliferation, And Security: How Does Green and Sustainable Chemistry Contribute?

BUXING HAN
Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, China
Catalysis in Green Chemistry

MIRABBOS HOJAMBERDIEV
Uzbekistan-Japan Innovation Center of Youth, Tashkent 100095, Uzbekistan
Institut für Chemie, Technische Universität Berlin, Germany
Mixed-Anion Photocatalysts for Energy Conversion and Environmental Remediation

AURELIA VISA[1*], BIANCA MARANESCU[1], LAVINIA LUPA[2]
[1]Institute of Chemistry "Coriolan Dragulescu", 24 M. Viteazul Ave, Timişoara - 300223, Romania,
[2] Faculty of Industrial Chemistry and Enviromental Engineering, University Politehnica Timisoara, 2 Piata Victoriei, 300006, Timisoara, Romania
Metal Organic Frameworks: Complexity and Diversity in Structures and Green Applications

PHILIP JESSOP
Queen's University, Dept. of Chemistry, 90 Bader Lane, Kingston, Ontario, K7L 3N6, Canada
CO_2-Switchable Materials

C. OLIVER KAPPE
Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria
Greening the Manufacturing of Pharmaceuticals Applying Continuous Processing Principles

KLAUS KÜMMERER
Institute for Sustainable and Environmental Chemistry, and ISC Research and Education Hub, Leuphana University Lüneburg, Lüneburg, Germany
Design of Chemicals and Pharmaceuticals for Environmental Mineralisation

HAORAN LI
Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, 38 Zheda Road, Hangzhou, 310027, P. R. China.
Aerobic Oxidation in Vitamin Industry

PETER LICENCE
School of Chemistry, University of Nottingham, United Kingdom.
Chemistry in-Vacuo: Suck It and See!

ZHIMIN LIU
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China
Ionic Liquids Catalyze Chemical Reactions

LILIANA MAMMINO
School of Mathematical and Natural Sciences, University of Venda, South Africa
Computational Chemistry and Green Chemistry. An Overview of Promising Synergies

ELENA POMARI
Department of Infectious-Tropical Diseases and Microbiology (DITM), IRCCS Sacro Cuore Don Calabria Hospital in Negrar di Valpolicella, Italy
Green Chemistry and Coronavirus

NATALIA TARASOVA
Dmitry Mendeleev University of Chemical Technology of Russia, Institute of Chemistry and Problems of Sustainable Development, UNESCO Chair in Green Chemistry for Sustainable Development, Miusskaya Sq., 9, Moscow 125047 Russia
Green Chemistry within Planetary Boundaries

KONSTANTINOS TRIANTAFYLLIDIS
[1] *Aristotle University of Thessaloniki, Department of Chemistry, University Campus P.O. Box 116, 54124 Thessaloniki, Greece*
[2] *Aristotle University of Thessaloniki, Center for Interdisciplinary Research and Innovation (CIRI), Balkan Center, 10th km Thessaloniki-Thermi Rd, P.O. Box 8318, 57001 Thessaloniki, Greece*
Integrated biorefinery for lignocellulosic biomass valorization to fuels, chemicals and polymers

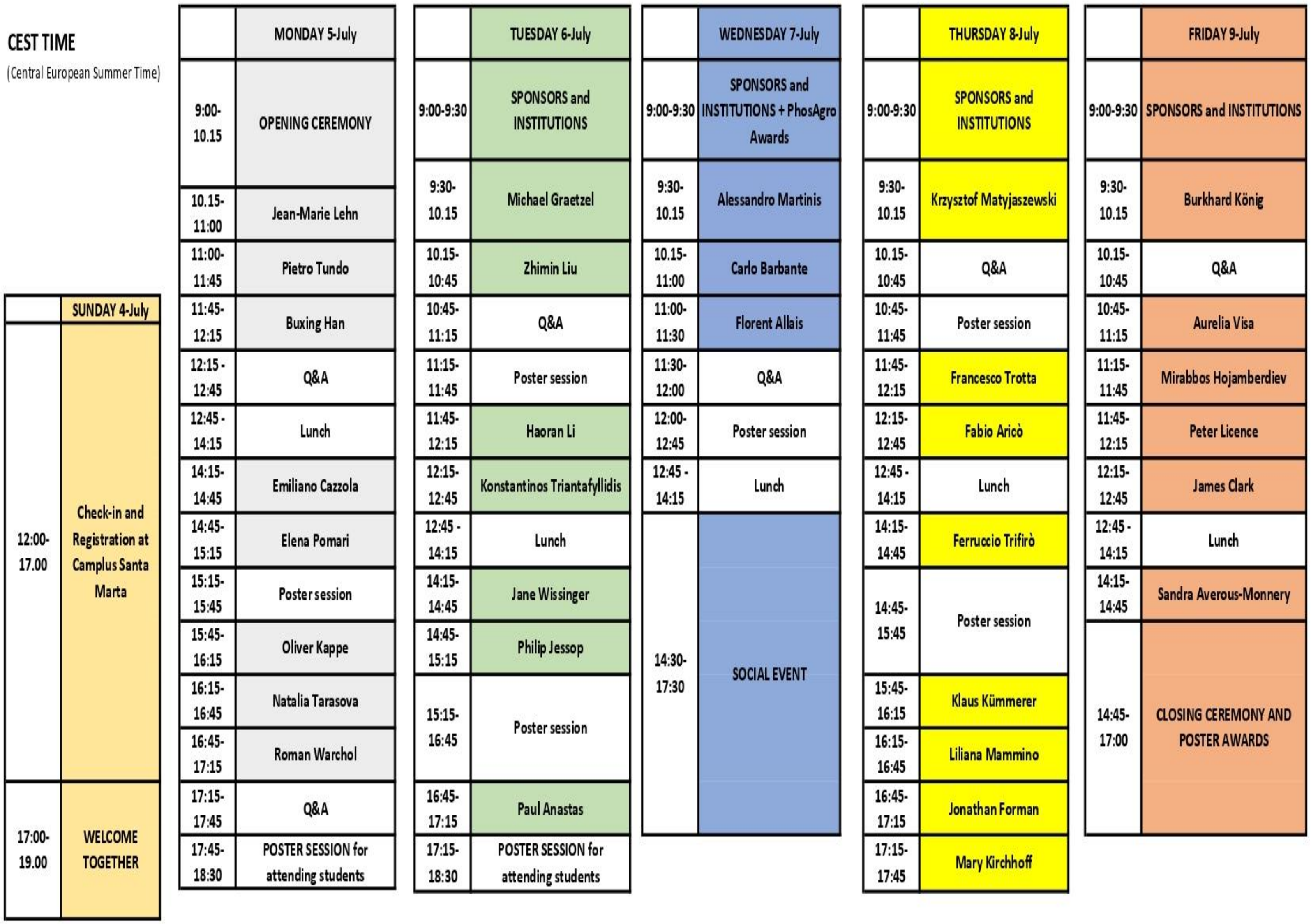
FERRUCCIO TRIFIRÒ
Professor Emeritus, University of Bologna and honorary founder of «Greeen Sciences for a Sustainable Development Fundation”
The Green and Sustainable Synthesis of Methacrylic Acid Methylmethacrylate

FRANCESCO TROTTA
Department of Chemistry, University of Turin. Via Pietro Giuria 7, 10125 Torino - Italy
Exploitation of Renewable Resources in Polymer Chemistry

ROMAN WARCHOL
International Cooperation Branch, International Cooperation and Assistance Division, Organisation for the Prohibition of Chemical Weapons (OPCW), Johan de Wittlaan 32, 2517 JR, The Hague, The Netherlands
Activities of the Organisation for The Prohibition of Chemical Weapons in Relation To Green Chemistry

JANE E. WISSINGER
University of Minnesota, Teaching Professor, 207 Pleasant St. SE, Minneapolis, MN, United States
Green Chemistry Curriculum: Training Chemists for a Sustainable Future

TIMETABLE



CEST TIME

(Central European Summer Time)

	SUNDAY 4-July
12:00-17.00	Check-in and Registration at Camplus Santa Marta
17:00-19.00	WELCOME TOGETHER

	MONDAY 5-July
9:00-10.15	OPENING CEREMONY
10.15-11:00	Jean-Marie Lehn
11:00-11:45	Pietro Tundo
11:45-12:15	Buxing Han
12:15 - 12:45	Q&A
12:45 - 14:15	Lunch
14:15-14:45	Emiliano Cazzola
14:45-15:15	Elena Pomari
15:15-15:45	Poster session
15:45-16:15	Oliver Kappe
16:15-16:45	Natalia Tarasova
16:45-17:15	Roman Warchol
17:15-17:45	Q&A
17:45-18:30	POSTER SESSION for attending students

	TUESDAY 6-July
9:00-9:30	SPONSORS and INSTITUTIONS
9:30-10.15	Michael Graetzel
10.15-10:45	Zhimin Liu
10:45-11:15	Q&A
11:15-11:45	Poster session
11:45-12:15	Haoran Li
12:15-12:45	Konstantinos Triantafyllidis
12:45 - 14:15	Lunch
14:15-14:45	Jane Wissinger
14:45-15:15	Philip Jessop
15:15-16:45	Poster session
16:45-17:15	Paul Anastas
17:15-18:30	POSTER SESSION for attending students

	WEDNESDAY 7-July
9:00-9:30	SPONSORS and INSTITUTIONS + PhosAgro Awards
9:30-10.15	Alessandro Martinis
10.15-11:00	Carlo Barbante
11:00-11:30	Florent Allais
11:30-12:00	Q&A
12:00-12:45	Poster session
12:45 - 14:15	Lunch
14:30-17:30	SOCIAL EVENT

	THURSDAY 8-July
9:00-9:30	SPONSORS and INSTITUTIONS
9:30-10.15	Krzysztof Matyjaszewski
10.15-10:45	Q&A
10:45-11:45	Poster session
11:45-12:15	Francesco Trotta
12:15-12:45	Fabio Aricò
12:45 - 14:15	Lunch
14:15-14:45	Ferruccio Trifirò
14:45-15:45	Poster session
15:45-16:15	Klaus Kümmerer
16:15-16:45	Liliana Mammino
16:45-17:15	Jonathan Forman
17:15-17:45	Mary Kirchhoff

	FRIDAY 9-July
9:00-9:30	SPONSORS and INSTITUTIONS
9:30-10.15	Burkhard König
10.15-10:45	Q&A
10:45-11:15	Aurelia Visa
11:15-11:45	Mirabbos Hojamberdiev
11:45-12:15	Peter Licence
12:15-12:45	James Clark
12:45 - 14:15	Lunch
14:15-14:45	Sandra Averous-Monnery
14:45-17:00	CLOSING CEREMONY AND POSTER AWARDS

PROGRAMME

MONDAY 5 JULY <u>MORNING</u>

9:00-10.15 OPENING CEREMONY

<u>Presenter:</u>

1. ICGCSD and GSSD Foundation – **Pietro Tundo:** Chair of Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation

2. Ca' Foscari University – **Salvatore Orlando,** Department of Environmental Sciences, Informatics and Statistics (DAIS) Director

3. IUPAC – **Christopher Brett:** IUPAC President and Professor at University of Coimbra

4. PhosAgro – **Andrey Guryev:** CEO of PhosAgro

5. International Council of Sciences - **Natalia Tarasova:** Mendeleev University of Chemical Technology of Russia

6. UNEP - **Sandra Averous-Monnery**, Programme Officer at the United Nations Environment Programme (UNEP)

1st SESSION:

<u>Moderator: Mirabbos Hojamberdiev</u>

10.15-11:00 **Jean-Marie Lehn**

11:00-11:45 **Pietro Tundo**

11:45-12:15 **Buxing Han**

12:15-12:45 Q&A

12:45-14:15 Lunch

MONDAY 5 JULY <u>AFTERNOON</u>

2nd SESSION:

<u>Moderator: Aurelia Visa</u>

14:15-14:45 **Emiliano Cazzola**

14:45-15:15 **Elena Pomari**

15:15-15:45 ***1st POSTER SESSION ONLINE***

3rd SESSION:

Moderator: Aurelia Visa

15:45-16:15 **Oliver Kappe**

16:15 -16:45 **Natalia Tarasova**

16:45-17:15 **Roman Warchol**

17:15-17:45 Q&A

17:45-18:30 ***POSTER SESSION for attending students***

TUESDAY 6 JULY MORNING

9:00-9:30 SPONSORS and INSTITUTIONS

EuChemS - **Ana Aguiar-Ricardo**, President of EuChemS Division on Green and Sustainable Chemistry
ICGCSD –**Buxing Han**, Secretary of the Interdivisional Committee of Green Chemistry for Sustainable Development

4th SESSION:

Moderator: Christopher Brett

9:30-10.15 **Michael Graetzel**

10.15-10:45 **Zhimin Liu**

10:45-11:15 Q&A

11:15 -11:45 ***2nd POSTER SESSION ONLINE***

5th SESSION:

11:45-12:15 **Haoran Li**

12:15-12:45 **Konstantinos Triantafyllidis**

12:45-14.15 Lunch

TUESDAY 6 JULY AFTERNOON

6th SESSION:

Moderator: Konstantinos Triantafyllidis

14.15-14.45 **Jane Wissinger**

14:45-15:15 **Philip Jessop**

15:15 -16:45 ***3rd POSTER SESSION***

16:45-17:15 **Paul Anastas**

17:15-18:30 ***POSTER SESSION for attending students***

WEDNESDAY 7 JULY MORNING

9:00-9:30 SPONSORS and INSTUTUTIONS

PhosAgro – **Alexander Antonov**

PhosAgro Awards for attending students

7th SESSION:

Moderator: Oliver Kappe

9:30-10.15 **Alessandro Martinis**

10.15-11:00 **Carlo Barbante**

11:00-11:30 **Florent Allais**

11:30-12:00 Q&A

12:00-12:45 ***4th POSTER SESSION***

12:45-14.15 Lunch

WEDNESDAY 7 AFTERNOON

SOCIAL EVENT

THURSDAY 8 JULY MORNING

9:00-9:30 SPONSORS and INSTUTUTIONS

OPCW - **Gaetano Carminati**, Senior Technical Expert from the National Authority for the Prohibition of Chemical Weapons

Ca’ Foscari BAS - **Alessandra Zorzi**, Director of Ca’ Foscari Library of Scientific Area

8th SESSION:

Moderator: Pietro Tundo

9:30-10.15 **Krzysztof Matyjaszewski**

10.15-10:45 Q&A

10:45 -11:45 ***5th POSTER SESSION***

9th SESSION:

11:45-12:15 **Francesco Trotta**

12:15-12:45 **Fabio Aricò**

12:45-14:15 Lunch

THURSDAY 8 AFTERNOON

10th SESSION:

Moderator: Fabio Aricò

14:15-14:45 **Ferruccio Trifirò**

14:45-15:45 ***6th POSTER SESSION***

11th SESSION:

Moderator: Fabio Aricò

15:45-16:15 **Klaus Kümmerer**

16:15-16:45 **Liliana Mammino**

16:45-17:15 **Jonathan Forman**

17:15-17:45 **Mary Kirchhoff**

FRIDAY 9 MORNING

9:00-9:30 SPONSORS and INSTUTUTIONS

Marco Bella – Member of Parliament of the Italian Republic in the Chamber of Deputies and Professor at La Sapienza University of Rome

12th SESSION:

Moderator: Francesco Trotta

9:30-10.15 **Burkhard König**

10.15-10:45 Q&A

10:45-11:15 **Aurelia Visa**

11:15-11:45 **Mirabbos Hojamberdiev**

11:45-12:15 **Peter License**

12:15-12:45 **James Clark**

12:45-14:15 Lunch

FRIDAY 9 AFTERNOON

13th SESSION:

Moderator: Pietro Tundo

14:15-14:45 UNEP - **Sandra Averous-Monnery**, Programme Officer at the United Nations Environment Programme (UNEP)

14:45-15:45 **Online Poster Winners Awards –** Pietro Tundo

15:45-16:15 Closing Ceremony

Closing Remarks

Pietro Tundo – Chair of the Summer School

Group Photo

SUMMER SCHOOL TOPICS

1. Exploitation of renewable resources
2. New reaction pathways
3. Energy saving
4. Food safety
5. Climate Change damages mitigation
6. Education
7. Health

ABSTRACTS OF PLENARY LECTURES

JEAN-MARIE LEHN

ISIS, Université de Strasbourg, France

PERSPECTIVES IN CHEMISTRY: MOLECULAR – SUPRAMOLECULAR – ADAPTIVE CHEMISTRY

Molecular chemistry has developed a wide range of very powerful procedures for mastering the organisation of matter and building ever more complex molecules from atoms linked by covalent bonds.

Supramolecular chemistry lies beyond molecular chemistry. It aims at constructing and implementing highly complex chemical systems from molecular components held together by non-covalent intermolecular forces. It relies on the development of pre-organized molecular receptors for effecting *molecular recognition*, catalysis and transport processes, on the basis of the *molecular information* stored in the covalent framework of the components and read out at the supramolecular level through specific interactional algorithms.

A further step consists in the design of systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components, thus behaving as *programmed chemical systems*. Chemistry may therefore also be considered as an *information science*, the science of informed matter.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. It takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

The implementation of these concepts points to the emergence of *adaptive* and *evolutive chemistry*.

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PIETRO R. TUNDO

Department of Environmental Sciences, Informatics and Statistics, Ca’ Foscari University, Venezia, and *President of Green Sciences for Sustainable Development Foundation, Venice*

REACTION MECHANISMS AND ENERGY PROFILES: HOW GREEN CHEMISTRY COMPLIES WITH THEM. THE CASE OF DIMETHYL CARBONATE

An important task for organic chemists toward a sustainable development is to discover and develop new reaction pathways in syntheses; they, coupled with metrics measurement, are the fundamental bases of green and sustainable chemistry.

Due to its benign nature, interest on Dimethyl Carbonate (DMC) has been enormously increasing in the last few decades: it is currently used in many chemical reactions as DMC can substitute chlorine-based chemistry. Green preparations of anti-inflammatory drugs, polymers, fragrances and solvents are widely reported. DMC peculiar reaction outcomes are based on its anisotropic electrophilic nature and because it follows exemplarily the Pearson’s HSAB theory; in doing that, DMC and Dialkyl Carbonates (DACs) give unprecedent selectivity.

Comparison among Esters and Carbonates reaction pathways is dramatic in nucleophilic attach as it proceeds very differently: in methyl acetate the reactions take place almost exclusively at the carbonyl sp^2 because S_N2 substitutions on the methyl sp^3 have a higher activation energy; in the dimethyl carbonate, instead, the nucleophilic attach to the sp^2 carbon is more difficult, while the attach to the alkyl carbon is easier; the activation energy of the S_N2 reaction pathway is further decreased by entropic factors if formation of cycles is involved (Figure).

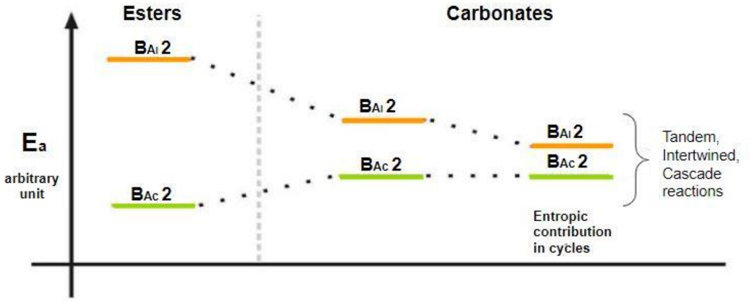

Figure. Activation energies in Esters and Carbonates; only $B_{Ac}2$ and $B_{Al}2$ reaction mechanisms are shown. Ingold’s terminology is adopted for esters and carbonates.

So, while in esters only sp^2 carbon is susceptible of a nucleophilic attack, in DACs Ea of $B_{Ac}2$ and $B_{Al}2$ are almost comparable; moreover, because the reagent is modified during the reaction, different reactions can take place in sequence in the same pot. Thus, tandem reaction, cascade, and intertwined reactions are possible in carbonates. This cannot occur in esters and wasn’t ever reported.

S_N2 Nucleophilic substitution reactions at saturated and acylic carbons will be discussed; they take place either in basic and acidic-catalyzed conditions and allowed to get > 99% in *mono*-methylation reactions at the methylene carbon. Heterocycles of 5 and 6 atoms were obtained in quantitative yields, thus opening the way to novel compounds through a green chemistry pathway.

Limitations and new results will be presented: when the formation of cycles occurs, and when it doesn’t. Moreover, also unimolecular substitutions take place.

Energy constraints and the dual electrophilic character of DACs originate unexpected reactivity and give results which are impossible for Esters.

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MICHAEL GRAETZEL

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MESOSCOPIC PHOTOSYSTEMS FOR THE GENERATION OF ELECTRICITY AND FUELS FROM SUNLIGHT

Learning from the concepts used by green plants photosynthesis, we have developed mesoscopic photosystems affording efficient solar light harvesting and conversion to electricity and fuels [1-4]. Solar cells using dyes, semiconductor quantum dots or perovskite pigments [5-8] as light harvesters have emerged as credible contenders to conventional silicon cells photovoltaic devices. Dye sensitized solar cells (DSCs) were the first to use a three-dimensional mesoscopic junction for solar electricity production. The power conversion efficiency for DSC's is currently 15.1 % in direct sunlight and 35 % in ambient light. DSCs are simple and relatively inexpensive to manufacture and they possess unique practical advantages including flexibility and transparency. These features along with excellent long-term stability have fostered first commercial applications large scale industrial production. Dye sensitized solar cell have engendered the advent of perovskite solar whose rapid efficiency rise from 3 % to over 25 % has stunned the photovoltaic community. Due to their exceptional performance, they are presently being intensively investigated as one of the most promising future PV technology. We have applied these fundamentally new concepts to realize highly efficient generation of hydrogen and reduction of carbon dioxide to ethylene by sunlight using water as electron source.

ALESSANDRO MARTINIS
Vice President
Danieli Centro Metallics
**Corresponding author: a.martinis@danieli.it*

LOW CARBON EMISSION GREEN STEELMAKING IS POSSIBLE

The EU initiatives to reduce the carbon dioxide emissions in the atmosphere and the worldwide attention to this subject require every sector of human activities to act quickly to reach this goal. Steelmaking industry is responsible for around 8% of the total GHG emissions and is one of the “hard to abate” sectors. There are ready available technologies, which allow to drastically reduce the CO2 impact of the steel production, among which the Direct Reduction of Iron Ores utilizing natural gas and, when available, hydrogen. The lecture will illustrate the present status of the technology and the challenges to migrate from Carbon based to Hydrogen based steel production.

CARLO BARBANTE
Institute of Polar Sciences and Ca' Foscari University of Venice
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TOO LATE FOR 2°C? FROM THE PARIS AGREEMENT TO THE CLIMATE OF TOMORROW

KRZYSZTOF MATYJASZEWSKI

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**Corresponding author:* matyjaszewski@cmu.edu

GREEN MATERIALS BY ATOM TRANSFER RADICAL POLYMERIZATION UNDER BENIGN CONDITIONS

Fundamentals of copper-based ATRP (atom transfer radical polymerization) will be presented. Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. To combat unavoidable radical termination, several techniques for the regeneration of the catalytic systems have been developed. They include various benign chemical reagents such as ascorbic acid or sugars but also external stimuli: electrical current, light, mechanical forces and ultrasound. ATRP can be carried out without organic solvents, in bulk and in aqueous media under homogeneous conditions or in dispersed media. Reducing agent permit the reaction without deoxygenation in the flasks open to air. This is additionally aided by enzymatic degassing systems.

The range of monomers for ATRP has been expanded to (meth)acrylates and acrylamides from renewable resources. They have been used for synthesis of well-defined polymers with precisely controlled molecular architecture with designed shape, composition and functionality. Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates were prepared with high precision. Some examples of nanostructured multifunctional hybrid materials for applications related to environment, energy and catalysis will be presented.

BURKHARD KÖNIG

Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany
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USING VISIBLE LIGHT FOR MORE SUSTAINABLE ORGANIC SYNTHESIS

Sensitized photochemistry evolved over the last 20 years into an enabling technology for the synthesis of complex organic molecules due to new mechanistic concepts and advances in light sources.[1] The use of visible light and dual catalytic systems allow now challenging transformations with good selectivity under mild reaction conditions.[2] Although light is an ideal reagent for chemistry (cheap, safe, can be used in large excess) it comes with certain limitations:

1. Compared to chemical bond energies, the energy of a visible light photon is small and photocatalytic activation of stronger bonds therefore requires special strategies.[3]

2. Photoinduced electron transfer leads to radical ions or combined with proton transfer to radicals, but the majority of chemical reactions proceeds via ionic intermediates. How can we generate reactive anions by light?[4]

3. Metal complexes and organic dyes are widely used as molecular photocatalysts in synthesis, but their stability and reuse can be problematic. Organic semiconductors are a valid alternative, particular for applications at larger scale.[5]

The lecture discusses approaches to overcome these and other current and future challenges in chemical photocatalysis.

DFG Deutsche Forschungsgemeinschaft German Research Foundation
erc European Research Council Established by the European Commission
GRK 1626 Chemical Photocatalysis
CRC 325

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ABSTRACTS OF LECTURES

FLORENT ALLAIS

Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France

BIOMASS UPGRADING THROUGH THE COMBINATION OF BIOTECHNOLOGY, GREEN CHEMISTRY & DOWNSTREAM PROCESS

Under the patronage of local communities (Conseil Régional Grand Est, Conseil Départemental de la Marne and Grand Reims), AgroParisTech has built the team "Industrial Agro-Biotechnologies" (URD ABI) devoted to the **valorization of biomass.**

To carry out its missions, URD ABI has built, **from October 2012, a multi-disciplinary team. With expertise in chemistry, microbiology, process and chemical engineering as well as analytical chemistry, URD ABI is able to conduct fundamental as well as applied multi-disciplinary research projects**.

Our ambition is to develop and optimize **sustainable industrial processes and high valued-added products from agro-resources** (e.g., biorefineries by-products, agro-waste). More precisely, the scientists aim at the development of **platform molecules from biomass** that will be used to develop **new functional bio-based additives, polymers or materials, but also valuable sustainable fine chemicals**.

Our strategy is based on the combination of different approaches such as:

- Identifying a promising biobased synthon and develop new (macro)molecules with innovative properties

- Devising a safer, cheaper, greener and biobased alternative to a known commercial compound

- Working with industrials to overcome their technological and/or scientific bottlenecks

Examples illustrating these approaches will be presented.

PAUL T. ANASTAS

Director of Photonics and Interfaces (LPI), Institute of Chemical Science and Engineering Faculty of Basic Science Ecole Polytechnique Federale de Lausanne, Switzerland

THE PERIODIC TABLE OF THE ELEMENTS OF GREEN AND SUSTAINABLE CHEMISTRY

The field of green chemistry has a more than twenty-five year history of invention and innovation of creating new materials, new products, new manufacturing processes that perform better and cost less while being sustainable and safe for humans and the environment. The range of products invented and improved by green chemistry touches virtually every industry sector from agriculture to energy to medicine to plastics to electronics. While the scientific brilliance that enables these discoveries and innovations are essential and necessary, they are not sufficient. In order for green chemistry to make positive impact on a scale and with the urgency necessary to address the greatest challenges of our time as enumerated in the United Nations Sustainable Development Goals, there will need to be a supporting structure. This structure is outlined in the Periodic Table of the Elements of Green and Sustainable Chemistry using the metaphor of the original Periodic Table first introduced 150 years ago, to present the enabling conceptual frameworks, metrics, legal/economic/policy drivers to advance and empower the transition to a more sustainable world.

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BIO-BASED PLATFORM CHEMICALS AND DIALKYL CARBONATES: A GREEN MATCH

In the last twenty years biorefinery has gained exceptional attention prompted by the need of substituting petroleum-based compounds with renewable one so to establish a bio-based economically self-sustained industry. The US Department of Energy (DOE) has published a list of 15 target molecules, namely "Top 10", that are considered of special interest for biorefinery development.[1] These compounds have been selected by taking into consideration factors such as available processes, economics, industrial viability, size of markets and their possible employment as a platform to produce derivatives.

Over the years, due to the considerable progress in biorefinery development, this list, as well as the criteria used to identify bio-based products has been revised. Several new compounds substituted the ones that have not received a great research interest. However, among the original selected chemicals, D-sorbitol, together with 5-hydroxymethylfurfural (HMF) derivatives still occupies a top position in the list as they encompass all of the desired criteria for a bio-based platform chemicals. In fact, these building blocks have found numerous applications in the synthesis of chemicals, materials, and bio-based polymers.

In this perspective, it is herein reported our recent work on the reactivity and upgrading of D-sorbitol, and HMF with organic carbonates employed as green reagents and solvents. Several industrially appealing products have been achieved with potential applications as high boiling green solvents (i.e. dimethyl isosorbide), biofuels candidates (2,5-bis-alkoxymethylfurans - BAMF) and monomers for bio-polymers [2].

Keywords: Biorefinery; Green chemistry; Organic carbonates; Carbohydrates

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GREEN RADIOCHEMISTRY: DREAM OR REALITY ?

Radiopharmaceuticals are medicinal products based on radioactive isotopes [1]. Those molecules are unique in showing metabolic processes and identify diseases growth and localization. Those probes are fundamental to combine the morphological structure of disease, obtained with CT or MR technique, to the metabolic pictures of the process at the base of the disease obtained with the PET (Positron Emission Tomography). PET images are obtained collecting radiation emitted from isotopes, present inside the radiopharmaceuticals, after their interaction and after their selective localization on the target tissue (e.g. tumor cell). This technology gives the possibility to evaluate the in-vivo tumor cell metabolism or, in presence of specific receptor, the interaction between receptor and radiopharmaceuticals to locate the malignant cell and characterize it [2]. This technique requires nuclear reactions, and consequently nuclear waste is necessarily produced. In the last years more and more processes were focused to reduce waste and to allow more environment friendly and green radiopharmaceutical production processes. This focus became necessary, especially today when the PET technique continues to grow and becomes one of the frontline techniques for tumors diagnosis; of course, the needs of radiopharmaceuticals is growing proportionally. Studies on waste management are at the base of important improvements on radiopharmaceutical production to achieve the same goals, like long term stability, fast reactivity and water reaction media [3]. All these requirements are common to the study for developing new radiopharmaceuticals based on water solution, with a fast kinetic and long-term stability on physiological environment.

Keywords

Green radiochemistry, nuclear waste, green improvement.

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JAMES CLARK

Professor of Chemistry at the University of York; Founding Director of the Green Chemistry Centre of Excellence and the Bio-renewables Development Centre, United Kingdom

BIO-BASED SOLVENTS AND THEIR SELECTION

Solvents are fundamental to many industrial processes but the replacement of many traditional but hazardous solvents is one of the greatest challenges in modern chemistry. Many common solvents are now known to present unacceptable levels of risk to the environment, workers and in some cases the general public. New chemicals legislation notably REACH is proving to be especially challenging with solvents including some dipolar aprotic amides being classified as substances of very high concern. We must assume that many of our workhorse solvents will not be available in the near future. In this lecture I will critically review the alternative solvents that are available to replace toxic or otherwise unacceptable solvents. In particular I will look at the emergence of bio-based solvents and how they can fit into a greener solvent landscape as well as support the growing bio-economy movement. My talk will include a study on a "sustainable solvent selection service" whereby solvent replacements are chosen in a rather more logical way than more familiar and serendipitous approaches. This relies on the importance of multi-parameter indicators of solvent polarities including those provided through the Kamlet-Taft solvatochromic parameters or Hansen solubility parameters. Case studies will be used to help illustrate how a new bio-based solvent can emerge from initial design through to commercialisation, upscaling and multiple sector applications.

JONATHAN E. FORMAN

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CHEMİCAL DİSARMAMENT, NON-PROLİFERATİON, AND SECURİTY: HOW DOES GREEN AND SUSTAINABLE CHEMISTRY CONTRIBUTE?

Harmful properties of chemicals have been exploited as weapons throughout the history of warfare. This history has also seen diplomatic efforts to limit, control, and/or completely ban certain weaponizable chemicals through international treaties and agreements. Within these agreements chemistry finds its way into the policy sphere, where it intersects with diplomatic efforts and legal obligations. This lecture will discuss chemicals of war, international arms control and disarmament agreements, and the obligations that impact upon them. The presentation will explore how chemistry influences policy, and where policy considerations and chemistry both challenge and support one another. In the context of “less hazardous” chemicals, it is often said that it is the dose that makes the poison, which can be a challenge to some of the objectives of green chemistry. A chemical may be designed to be “less harmful”, and developed for peaceful and benign purposes, but does this reduce or remove the risk that such a chemical might be used maliciously by those with harmful intent? In the context of the Green Chemistry Postgraduate Summer School, students will be asked to consider chemical security in a green and sustainable chemistry context, how developments in this field support the norms of chemical disarmament and non-proliferation, and where the needs of chemical security and the aspirations of green chemistry compliment as well as diverge from one another.

BUXING HAN

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CATALYSIS IN GREEN CHEMISTRY

It is known that most reaction processes need catalysts. Thus, catalysis plays a crucial role in green chemistry. Green catalysts should have some typical characteristics, such as high activity, selectivity, and stability, nontoxic, green preparation process using abundant feedstocks, good reusability. Carbon dioxide (CO_2) is the main greenhouse gas, and it is also a renewable, abundant, and cheap C_1 feedstock. Biomass is abundant renewable carbon resource. Use of biomass and CO_2 as carbon source to produce fuels and value-added chemicals is of great importance for the sustainable development of our society. In recent years, we are very interested in catalytic conversion biomass and CO_2. In this presentation, I would like to discuss some of the recent results in our group on design of green catalysts and their application in conversion of biomass and CO_2 into valuable chemicals and fuels [1-11].

Keywords: Green Catalysis, Transformation, Biomass, Carbon dioxide, Chemical, Fuel

Acknowledgements

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ARTIFICIAL PHOTOSYNTHESIS – GREEN CHEMICAL PROCESS FOR GREEN HYDROGEN PRODUCTION

The depletion of fossil fuels, serious environmental problems, and growing energy demand urge a modern society to develop and exploit clean and renewable energy sources. As a replica of natural photosynthesis, semiconductor-based artificial photosynthetic system is regarded as one of the most economically viable and green chemical processes to produce renewable hydrogen energy from solar water splitting and to remove organic pollutants. To efficiently utilize solar energy in the wide visible range, it is necessary to enhance the visible-light-driven photocatalytic performance of the known photocatalysts and to discover novel visible-light-active photocatalysts. We have successfully developed an NH_3-assisted direct flux growth approach to reduce the density of intrinsic defects in transition metal oxynitrides ($BaTaO_2N$, $BaNbO_2N$, $LaTiO_2N$, etc.), which led to the substantial enhancement in solar water splitting activity. New Dion-Jacobson phase $CsBa_2Ta_3O_{10}$ was discovered, and two-dimensional oxynitride nanostructures with high crystallinity, less defect density, and high photocatalytic activity of $CsBa_2Ta_3O_{10}$, $KLaTiO_4$, and $K_2La_2Ti_3O_{10}$ were synthesized. Our work revealed new insights into why creating a *p-n* heterojunction using bismuth oxyhalides (BiOCl, BiOI) and doping are important for bandgap engineering and enhancing the photocatalytic activity of less active photocatalysts. As an emerging class of inorganic materials, mixed-anion compounds have potential applications in green energy conversion and environmental remediation.

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METAL ORGANIC FRAMEWORKS: COMPLEXITY AND DIVERSITY IN STRUCTURES AND GREEN APPLICATIONS

The research carried out in the field of green chemistry is governed by twelve principles. High need to develop new materials, processes and systems that mitigate or eliminate the use and generation of hazardous substances is urgently needed.

A high study class of complex structured porous materials, metal-organic frameworks (MOFs), composed of different central metal nodes bridged by organic linkers, are an intriguing class materials are deeply studied for various environmental applications.

The complexity and diversity of architectural structures of MOFs provide unique properties as high thermal, chemical and mechanical stability, large pore sizes with applications in numerous areas such as catalysis, gas storage, solar energy conversion, drug delivery, adsorption and separation for air and water pollution remediation.

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CO_2-SWITCHABLE MATERIALS

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Switchable materials are so common in our everyday lives that we rarely appreciate how green they are. We switch on the lights when we enter a room because we need the illumination, but we switch off the lights when we exit in order to save energy. The switchability of lights makes them greener and less energy-consuming than non-switchable lights would be. But should we not demand the same from our solvents, surfactants, drying agents, and coatings? A switchable solvent, one that dissolves a solute when needed and later releases the product when dissolution is no longer wanted, could make processes more efficient and less environmentally harmful. Switching the solvent "off" would precipitate the product without the solvent needing to be removed by energy-intensive distillation. Perhaps such a solvent could also be more easily recycled? Similar arguments can be made for the expectation that many switchable materials could be greener than their non-switchable predecessors. However, if the switchable material is highly toxic or the trigger used to switch the material causes pollution, then the technology will not benefit the environment at all.

This presentation will describe the advantages and disadvantages of several triggers for switchable materials, and then describe the chemistry and selected applications of CO_2-switchable materials. Examples of the widely varying problems that could be addressed by using CO_2 as a modifier include the following:

- nearly half of worldwide use of organic solvents is in paints and coatings, because water-based coatings are inferior.
- about 1/3 of the world's rubber crop is thrown away every year due to coagulation before processing, so that the environmental impact of the remaining natural rubber is increased by 50%
- 1/3 of the world population is suffering from fresh water shortages and yet industries are seeking more places to discard their wastewater.
- conversion of biomass into chemical products usually requires energy-intensive separation of the product from water. Could CO_2 be used to facilitate that separation?

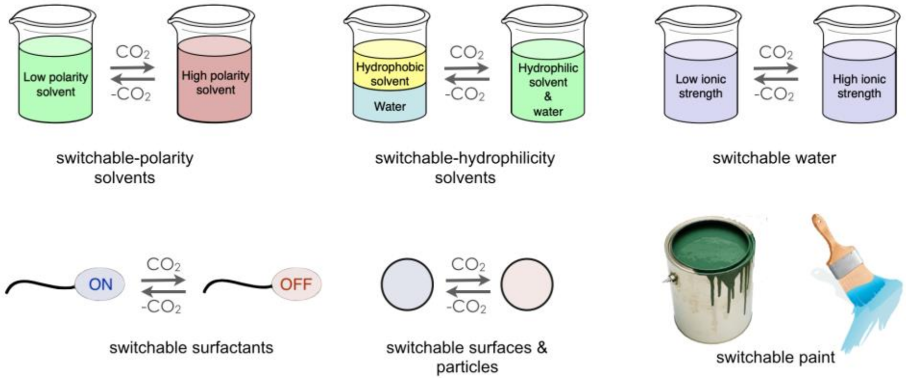

Figure 1. Some of the classes of CO2-switchable materials.

Keywords
carbon dioxide; solvent; surfactant; surface; coatings

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GREENING THE MANUFACTURING OF PHARMACEUTICALS APPLYING CONTINUOUS PROCESSING PRINCIPLES

Enhanced heat and mass transfer, precise residence time control, shorter process times, increased safety, reproducibility, better product quality and easy scalability are just a few of the advantages of flow chemistry and reason for the increasing implementation of continuous processes not only in academia but also into the fine chemical manufacturing sector. Notably, to make a process greener and more sustainable becomes eminently important when going from lab-scale to production scale. In this presentation, the question to which extent continuous flow processing has an impact as green technology, in particular on the synthesis of active pharmaceutical ingredients (APIs) on manufacturing scale, is discussed [1,2]. Based on the principles of both green chemistry and green engineering selected continuous processes are evaluated (Figure 1).

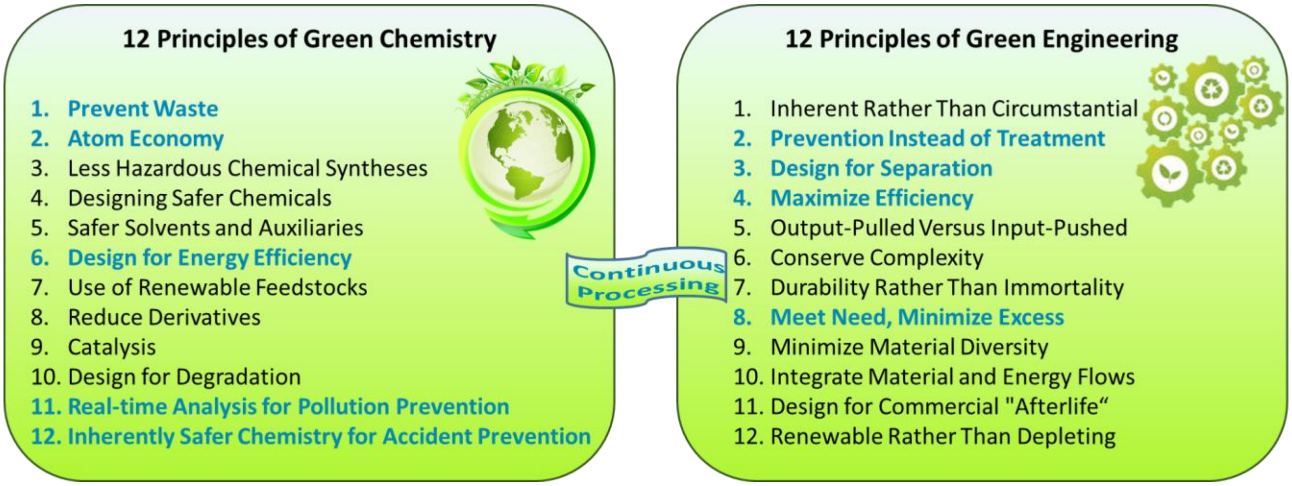

Figure 1. Twelve principles of green chemistry and green engineering and the impact of continuous processing highlighted in blue [2].

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DESIGN OF CHEMICALS AND PHARMACEUTICALS FOR ENVIRONMENTAL MINERALISATION

Pharmaceuticals and many chemicals are used in open applications such as personal care products, disinfectants, pesticides detergents or are released form products within their lifecycle into the aquatic environment such as plsiziser, flame retardants whiteners UV absorbers and many others. Such products and their constituents cannot be circulated within a circular economy (1). Only 20% or world's effluents are treated (2). However, even if there is treatment it does remove often a minor share of the water pollutants only. Furthermore, it has been found that advanced effluent treatment that is under discussion because of the limitations of conventional treatment can neither remove the majority of the pollutant. In contrast chemical treatment (e.g. advanced oxidation) often generates products of incomplete mineralisation (transformation products, TPs) that are most often unknown with respect to structure, fate and toxicity (3). It has been found however, that some are even more toxic than the parent compounds (4,5). Therefore, measures for input prevention at the source ("beginning of the pipe") are urgently needed (1). The molecules and their properties are at the very beginning of the pipe.

Design for environmental degradation (green chemistry principle #10) addresses this. However, complete mineralisation has to be reached in the best case to avoid follow up-problems caused by unwanted products of incomplete mineralisation, so called transformation products. In the presentation it will be demonstrated that this is feasible and how by applying several different methods for computational chemistry, analytical chemistry, toxicology and environmental microbiology (6-10).

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AEROBIC OXIDATION IN VITAMIN INDUSTRY

Vitamins are essential compounds for life, which play an important role in metabolic function. The artificial synthesis of vitamins has been well developed during last few decades [1], among which the aerobic oxidation is an emerging and flourish field. Using O_2 as the oxidant, the aerobic oxidation is a potential green process with high E-factor, however, it is challenging to control the selectivity.

Herein, we introduce three applications of aerobic oxidation in vitamin industry (Figure 1), including the oxidation of beta-isophoron in petrochemical process for vitamin E production [2], the oxidation of 2,3,6-trimethylphenol in coal chemical process for vitamin E production [3-4], and the oxidation of acetyl-cholesterol in vitamin D3 production [5]. The development of green and efficient catalyst system will be focused, and we will show the progress of mechanistic study on these reactions.

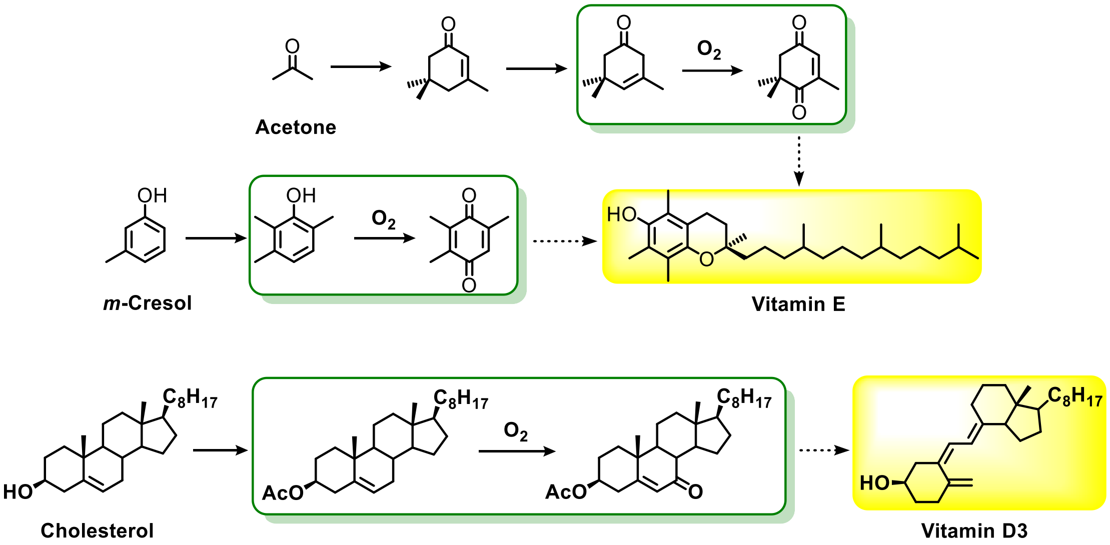

Figure 1. The brief industrial routes for production of vitamin E and vitamin D3.

Keywords: aerobic oxidation, vitamin E, vitamin D3, catalysis, mechanism

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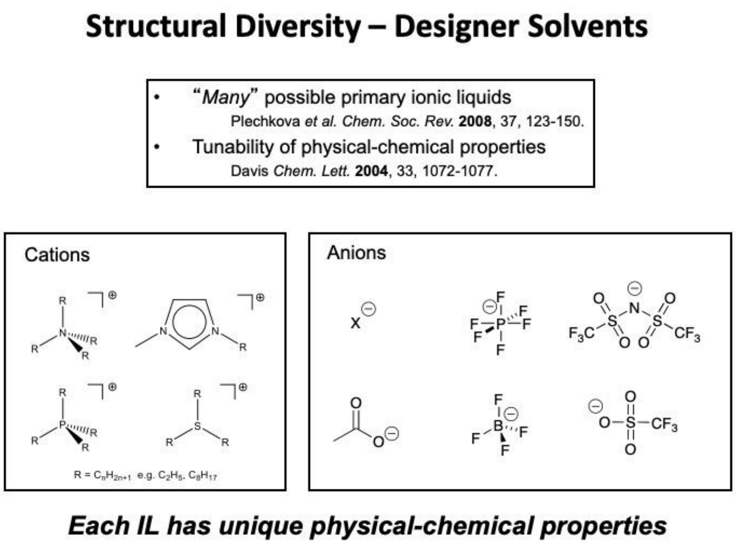
CHEMISTRY IN-VACUO: SUCK IT AND SEE!

Room Temperature Ionic Liquids are sterically hindered organic salts that exhibit melting points below the boiling point of water. Because they are composed entirely of ions, ionic liquids have almost zero vapour pressures and do not evaporate even under vacuum! This feature set alongside the large liquid-ranges observed for many ionic liquids has led to them being characterised as Green Solvents. Furthermore, structural diversity in the ionic components that can be brought together to form simple binary salts and mixtures, each with a unique set of physical and chemical properties, has led to them becoming known as designer solvents which could, in principle, be designed or engineered with a specific reaction of process in mind.



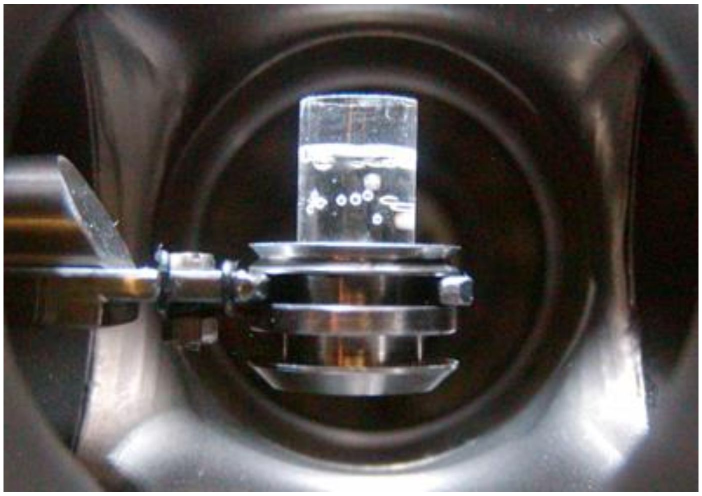
Structural Diversity – Designer Solvents

- "*Many*" possible primary ionic liquids
  Plechkova *et al.* *Chem. Soc. Rev.* **2008**, 37, 123-150.
- Tunability of physical-chemical properties
  Davis *Chem. Lett.* **2004**, 33, 1072-1077.

Each IL has unique physical-chemical properties

This lecture will give an overview of the basics physical chemistry that underpins the field of ionic liquids based chemistry, I will challenge the perception that these liquid solvents are indeed green and attempt to give examples where ionic liquid based technologies deliver advantages that may not be achieved using more traditional solvent systems.

I will explore opportunities to control chemistry via systematic ion choice and demonstrate the designer nature of simple systems to control physical parameters.
I will close with a brief overview of the impacts of science-based research across multiple scales, including a whole laboratory scenario.



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IONIC LIQUIDS CATALYZE CHEMICAL REACTIONS

Ionic liquids (ILs) are totally composed of organic cations and organic/inorganic anions, which can be designed with green features and specific functions, and thus showing promising applications in many areas. In chemical reaction process, ILs can be used as solvents, catalysts, or additives due to the existance of multiple interactions such as electrostatic force, Van der Waals force, hydrogen-bonding interaction, acid-base interaction, hydrophilic/hydrophobic interaction, π-π interaction and so on. Especially, stronger hydrogen-bond interactions exist between ionic and molecular/ionic species due to the presence of electrostatic forces. In this lecture, I will present our recent work on IL-catalysed chemical reactions.

We designed task-specific ILs that can chemically capture and activate CO_2 via forming anion-based carbonate or carbamate intermediates, and further accomplished its transformation to a series of heterocycles including quinazoline-2,4(1H,3H)-diones, cyclic carbonates, 2-oxazolidinones, oxazolones and benzimidazolones under metal-free conditions.[1-2] We proposed cooperative catalysis strategy of hydrogen bond donor and acceptor of ILs for chemical reactions, in which the cation as H-bond donor and anion as acceptor cooperatively catalyze various chemical reactions, such as the ring-closing C-O/C-O bond metathesis reactions of aliphatic diethers to O-heterocycles, the dehydrative etherification of alcohols to ethers, direct oxidative esterification of alcohols to esters.[3,4] In addition, we developed a series of IL-metal catalytic systems, and realized the reductive transformation of CO_2 to value-added chemicals.[5] The reaction mechanism has been explored in details. In summary, ILs can play multiple roles in chemical reaction processes, which have bright future in green chemistry.

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COMPUTATIONAL CHEMISTRY AND GREEN CHEMISTRY. AN OVERVIEW OF PROMISING SYNERGIES

Green chemistry envisages the design of environmentally benign substances and processes; the design of processes, in turn, also entails the design of substances that might be needed for their realization. Designing new substances with desired properties means designing their molecules; the prediction of the properties of the new molecules enables realistic predictions of the properties of the new substances even before they are synthesised. Furthermore, understanding the properties of the molecules of existing substances may help using them in more efficient ways or finding additional uses that might be beneficial. Computational chemistry is the area of chemistry which studies the properties of molecules; therefore, are many issues for which computational chemistry can provide information relevant for green chemistry. The lecture offers an overview of the green chemistry objectives and practices which entail molecular design, and highlights the types of information that can be contributed by computational chemistry research and their usefulness. The overview is supported by the consideration of concrete examples, leading to the conclusion that synergies between the two areas can enable interesting and fruitful outcomes.

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GREEN CHEMISTRY AND CORONAVIRUS

The novel coronavirus pandemic has rapidly spread globally since December 2019 with a dramatic effect on the world. As a matter of urgency, science communities have been commissioned to develop new methods for SARS-CoV-2 detection and therapeutics. Research has promptly focused on designing cures, vaccines and various techniques for viral detection including molecular methods such as reverse transcription polymerase chain reaction, droplet digital PCR, whole genome sequencing, tomography, optical biosensors and point-of-care diagnostics. Indeed, innovative technologies are required in order to provide a more accurate, sensitive and rapid diagnosis of SARS-CoV-2 to manage the outbreak. Furthermore, the use of green synthesized nanomaterials could leads to sustainable and environmentally friendly approaches for addressing this crisis. Novel viral outbreaks may occur in the future, and it is necessary to have virus sensitive technology to help detection and to reduce virus spread. Detection of pathogens in environmental surveillance and risk monitoring for pandemic control is essential.

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GREEN CHEMISTRY WITHIN PLANETARY BOUNDARIES

Green chemistry may become an efficient tool for overcoming chemophobia and agrochemophobia as a variant of it. It is not a new, earlier unknown, trend. It is rather a compact formulation of thinking principles for well-trained and socially responsible chemists–scientists or technologists. The latter thesis is confirmed by the active practical application of green chemistry approaches in industry including in Russia. However, not only the business community, but also top-level politicians have begun to try to follow this way of thinking. The United Nations has pointed out that green chemistry is a key science development trend. When increasing the productivity of crops, protecting them from pests, manufacturing new materials and products, developing transport, and creating medicines, humanity has caused unintended harm to the planet. In this connection, scientific papers devoted to the exhaustion of natural resources and the negative effect of human activity on the environment began to appear in the 1960s–1970s. According to some nonprofit organizations, such as the Global Footprint Network and the World Wildlife Fund, the consumption of natural resources for more than 40 years beginning from 1970 has exceeded the capability of our planet for their reproduction. This has led to a deficit in biocapacity, which is the capability of Earth's ecosystems to reproduce certain biomaterials and utilize the wastes of anthropogenic activity. According to the estimates of ecologists, in 2018, the needs of humanity exceeded the capabilities of nature by 1.5 times. In 2019, the Earth's annual resources were exhausted on July 29. Upon continuation of this trend, three planets like the Earth would be required to satisfy the needs of humanity by the year 2050. A logical continuation of scientific knowledge accumulation is the concept of sustainable development, according to which economic and social development must be combined with the preservation of nature, i.e., the protection of the structure, functions, and diversity of the Earth's natural systems. The notion "planetary boundaries" has come into common use [1]. This field has actively been under development for the past ten years. Nine planetary boundaries, including climate change, loss of biodiversity, and change in terrestrial ecosystems have been described [2]. Numerical values were established for most boundaries. However, all the attempts to give quantitative estimates for the limits of the chemical pollution and aerosol content in the atmosphere have not yet given any results [3]. It has not been possible to calculate what amount of contaminants can lead to irreversible changes in the biosphere. Neither it was possible to determine the future of aerosols and their ultimate content safe for the planet in the atmosphere. This uncertainty, in our opinion, may be considered as one of the reasons for the rise of chemophobia. Let us note that chemophobia, as well as any other phobia, cannot favor sustainable development. A cure for this disease is total chemical literacy formed beginning with one's school days and the responsible handling of chemicals, including their household use. The principles of green chemistry should become a code of conduct for specialists in chemistry who have graduated from institutions of higher education [4].

Keywords: planetary boundaries, chemophobia, green chemistry, chemical compounds, chemical literacy

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INTEGRATED BIOREFINERY FOR LIGNOCELLULOSIC BIOMASS VALORIZATION TO FUELS, CHEMICALS AND POLYMERS

The environmental pollution due to the intensive use of fossil fuels and their projected depletion have motivated research and development towards the utilization of alternative sources of energy/fuels and chemicals. Lignocellulosic biomass from agricultural/forestry residues, wood and food processing industry and municipal wastes, as well as dedicated non-edible crops, is considered as a sustainable solution. Within the “biorefinery” context, a “whole biomass” valorization approach is targeted, towards the production of value-added fuels, chemicals and polymers by applying atom and energy efficient “green” processes with minimum environmental impact.

In the present lecture, specific case-studies of individual processes that comprise an integrated biorefinery scheme for converting lignocellulosic biomass to valuable products are described. The first important step comprises of efficient pretreatment of biomass which aims to its selective fractionation into its main structural components (biopolymers): cellulose, hemicellulose and lignin. This can be achieved by “green” hydrothermal treatment (HT) in pure H_2O or by very dilute acid HT leading to hemicellulose removal and its partial hydrolysis to xylan/xylose and further conversion to furans (furfural, HMF) and acids (acetic, formic, levulinic, lactic) depending on the severity of the process [1,2]. Furfural, being one of the top bio-derived platform chemicals, can be further converted via catalytic hydrogenation to valuable furanic compounds (i.e. furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, etc.) [3] with high potential in the solvent, polymer and fuel industry.

The HT pretreated biomass (i.e. the cellulose part) is more susceptible to enzymatic hydrolysis compared to parent biomass towards glucose which can be utilized for the production of a wide spectrum of chemicals and fuels, such as 2nd generation bioethanol/butanol, succinic and lactic acids, levulinic acid and levulinates, sugar alcohols, etc. When a simple step of mild extraction of the formed surface lignin is applied, enzymatic digestibility of cellulose can be substantially increased [4]. Alternative routes to enzymatic or acid hydrolysis of cellulose, include the direct hydrolytic hydrogenation of cellulose towards sugar alcohols (i.e. sorbitol) and smaller diols/glycols [5].

The remaining lignin enriched solid (i.e. enzymatic hydrolysis lignin) after enzymatic hydrolysis of the HT pretreated biomass can be utilized towards the production of alkoxy/alkyl phenolics by fast pyrolysis or catalytic hydrogenolysis, as well as BTX monoaromatics and naphthalenes by catalytic fast pyrolysis, applying in both processes the appropriate catalysts [6-8]. The lignin-based bio-oils can be also further upgraded via hydrodeoxygenation towards (cyclo)alkane drop-in hydrocarbon fuels. Alternatively, these phenolic bio-oils can be utilized in the production of phenol-formaldehyde resins replacing, at least partially the petroleum-based phenol.

Whereas all the above biorefinery processes involve depolymerization and upgrading chemo/bio-catalytic reactions, the cellulose and lignin recovered at the various steps have the potential to be utilized as reactive additives in bio-based polymer (mainly epoxy and PF resins) composites, in the form of (nano)cellulose or (nano)lignin, with or without prior functionalization, offering additional valuable properties to the base polymers.

Keywords: lignocellulosic biomass; biorefinery; chemicals; fuels; polymers

Acknowledgements

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THE GREEN AND SUSTAINABLE SYNTHESIS OF METHACRYLIC ACID METHYLMETHACRYLATE

I shall speak of the synthesis of methacrylic acid (MAA) and methylmethacrylate(MMA) ,two chemical products for which an high number of alternative synthesis from different raw materials have been proposed, in order to realize a “Green and Sustainable Production”. MAA is used essentially to produce MMA, while the primary application for MMA, which represents approximately 50% of global demand, is as a feedstock for production of polymethylmethacrylate (PMMA) a transparent plastic with tradename is Crylux, Plexiglas, Perspex, Acrylite, Astariglas and Lucite. The second largest application of MMA is the production of paints and coatings, which consume about 40 % of its global demand. The first industrial process and the main process used to day to produce MAA and MMA is called «ACH» and it is realized through the production of acetone cyanohydrin from acetone and HCN, and after by reaction with H_2SO_h are forming methacrylic acid and high amount of NH_4HSO_4 and this process it is one of the most dangerous one used in the industry. The alternative industrial production of MAA and MMA are a lot of processes and many others have been also proposed but not yet realized in the industry. The first industrial process called the “acetone cyanohydrin” (ACH) has been created in 1937 and now days 60% of MAA and MMA in the world are produced with this process ,30% is produced from isobutene and 10% from ethylene. The disadvantages of the ACH process are the followings: the reagents are not raw materials and therefore they must be synthesized; it used HCN as reagent an high toxic substance, which is an historic chemical weapon; it is produced as intermediate acetone cyanohydrin a very toxic substance, that in presence of traces of H_2O liberates HCN; it is used high amount of H_2SO_4 , a corrosive substance that it creates also undesired polymerization, that reduces yield and can cause technical problems in plants and for this reason they must be strongly improved; it is produced as coproduct NH_4HSO_4 (1.2 kg for 1kg of MMA) that it can be a toxic waste or a toxic co-product to be purified . In the past it has been introduced in the sea or inside the land as waste (after it was forbidden). It has been used as fertilizer, but it is a toxic substance because it contains organic compounds (for this reason it has been forbidden) and it can be purified to produce again H_2SO_4 and this is a very expensive procedure. The alternatives to the ACH process are its modifications and the use of other raw materials and new processes. The modifications of ACH process are the followings: elimination only of the use of HCN with a change of only the first step of “ACH process”; elimination of the use of H_2SO_4 , transforming acetone cyanohydrin to methacrylic acid without the use of H_2SO_4.. The use of new processes is realized by elimination of the use both of HCN and H_2SO_4 , avoiding the production of NH_4HSO_4 with the following processes: the use of olefins (ethylene, propylene and isobutene) as raw materials; the use of C4 by-products of other chemical reaction as raw material; the use of biomass as raw materials; the depolymerization of wastes of polymethylmethacrylate to MMA. There are four types of processes from ethylene with following different first intermediates: propionic acid; methyl propionate, propionaldehyde, and propionic anhydride.From propylene it has been proposed two routes, through isobutyric acid and through propyne, but there not yet industrial processes, the only one is the ACH. From isobutene is forming methacrolein that after is oxidized directly to methyl methacrylate o through the formation of methacrylic acid. From biomass there are two technologies for MAA and MMA synthesis: the production of new raw materials for new technologies of synthesis and the building of new plants or the production from biomass of the some raw materials that are actually used to produce them from fossil fuels, therefore it will be no modification of their plants of production. Polymethylmethacrylate is one o the few polymers that can be depolymerized through a radical mechanism. The depolymerization occurs by heating at T 350-4OOC giving high yield of monomer (MMA) with high purity (95%).

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EXPLOITATION OF RENEWABLE RESOURCES IN POLYMER CHEMISTRY

To face severe environmental and health concerns, limit greenhouse effects and improve the management of the foreseeable depletion of fossil resources, over the last decades, chemistry has moved towards the use of renewable resources for the production of energy and the synthesis of chemicals. Unlike materials deriving from fossils, which are often concentrated in a limited part of the world, renewable raw materials can be produced and utilized theoretically everywhere. These renewable raw materials come from various value chains, such as vegetable oils, fats, cellulose, starch, wood and biomass. It is important to underline that, where possible, renewable raw materials coming from agricultural and forestry products should not be used for food or feed but expressly employed for the production of materials, heat, electricity or fuel. Today many products are made from renewable raw materials, which often require less energy consumption and use safer and ecofriendly synthetic routes. These include textiles, cosmetics, medicines, building materials, dyes, lubricants, intermediates and (bio)-polymers [1].

Of particular interest is the production of polymer materials using renewable resources. In fact, polymers have a wide range of applications and are of crucial importance in modern society. In 2015 a global production of 322 million tons of different polymers was recorded. However, only 1% is actually related to bio-polymers although a constant growth has been detected.

In this lesson I would like to share the results obtained over the last decades on the use of some starch derivatives i.e. cyclodextrins and linear dextrins to produce both cross-linked and branched polymers with an impressive number of applications [2]. Toxic solvent-free production and even solvent-free synthesis are possible, thus making these new materials particularly appealing.

Keywords: Raw materials, renewable resources, starch derivatives, dextrins, cyclodextrins

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ACTIVITIES OF THE ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS IN RELATION TO GREEN CHEMISTRY

Article XI of the Chemical Weapons Convention provides for the international cooperation between States Parties in the areas of chemistry for peaceful purposes to stimulate the economic and technological development of chemistry. The rationale is to facilitating the right of States Parties to conduct scientific research, develop, store, produce and transfer chemicals for peaceful purposes. By doing so, the Convention offers tangible benefits in addition to restrictions and obligations. Within this mandate and as part of the vast portfolio of its international cooperation programmes, the Technical Secretariat of the OPCW looks into building capacity of institutions, facilitating good practices and offering education and training in some fields of chemistry. This work engages multiple stakeholders including research and academia, industry, National Authorities (NA) and other governmental entities.

Among such priority fields, which contribute to the OPCW mission of preventing re-emergence of chemical weapons and promoting safety, security and sustainability across the life chain of chemicals, there is green and sustainable chemistry. The latter, on one hand, provides concrete solutions for the replacement of potentially vulnerable processes or chemicals from the safety and security point of view. On the other, it nurtures the culture of sustainability and related professional ethics in the growing generations of chemists.

The OPCW has been supporting Green and Sustainable Chemistry for a number of years. The original focus was on related scientific research, mobility of researchers, education and dissemination of scientific information in the field. More recently in 2016, the Green Chemistry Initiative came into place which provided a forum for discussion among stakeholders on best practices of green and sustainable chemistry in providing solutions for safety and security and on the role of the OPCW in supporting such developments in cooperation with partners.

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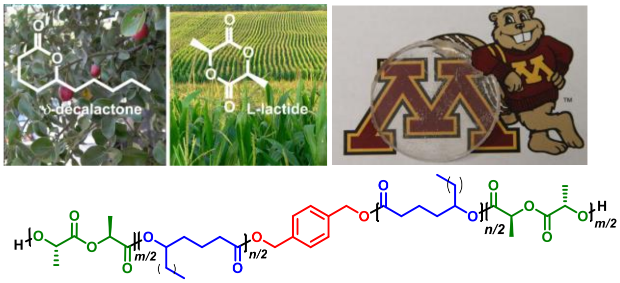
GREEN CHEMISTRY CURRICULUM: TRAINING CHEMISTS FOR A SUSTAINABLE FUTURE

This presentation will share how incorporation of green chemistry experiments into an introductory organic chemistry laboratory course over fifteen years ago at the University of Minnesota (U of MN), United States, has proliferated into many diverse and far-reaching educational programs. The topic of green chemistry immediately captured the interest of undergraduate students and graduate teaching assistants (TAs) who were inspired by green chemistry's "benign by design" approach to minimize environmental impact, reduce waste, and improve safety of chemical syntheses. This catalyzed research efforts to develop new green curriculum materials spearheaded by these students who could then see their efforts excite new classes of students in green chemistry practices.

As a Principle Investigator of the NSF Center for Sustainable Polymers, special emphasis was placed on curricula that translated new and current research in the area of environmentally friendly polymers to the classroom. Our experience showed that the topic of plastics and their negative impact on the environment is one that resonates strongly with students at all levels of education. A portfolio of experiments will be presented that illustrate polymers: a) synthesized from renewable or waste feedstocks; b) prepared using green processes, and/or; c) designed for degradation (Figure 1). We capitalized on the tunable properties of polymeric materials for student engagement through mechanical and physical property testing as well as the opportunity for incorporating guided-inquiry pedagogy.

Green and sustainable chemistry initiatives have since expanded across our department through a popular senior level green chemistry course, safety programs, outreach programs, green engineering applications, and teacher workshops. Curriculum content includes a wide range of topics from sustainable nanomaterials to social justice and health equity. This illustrates the multi-disciplinary nature of green chemistry and the connections students then make between the UN Sustainable Development goals, a systems thinking approach to discovery, and chemistry's role in achieving a sustainable future.



poly(L-lactide)-*block*-poly(δ-decalactone)- *block*-poly(L-lactide)

Figure 1. Sustainable Polymer Teaching Lab Experiment

Keywords
green and sustainable chemistry education
laboratory experiments
sustainable polymers
UN Sustainable Development Goals
systems thinking

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STUDENTS’ ABSTRACTS

The Abstracts are divided by topics and sorted in alphabetical order.

The Summer School Topics are the following:

1. Exploitation of renewable resources
2. New reaction pathways
3. Energy saving
4. Food safety
5. Climate Change damages mitigation
6. Education
7. Health

The legend below explains the participants’ contribution with their work to the Summer School: one star for those who sent their abstract, two stars for those who sent their abstract and poster, three stars for those who sent their abstract and poster and gave an oral presentation of their poster.

Those marked with four stars are the winners of the Poster Awards: six participants were selected by the Scientific Jury and gave an oral presentation on their work.

Legend:

★ **Only Abstract**

★★ **Abstract and Poster**

★★★ **Abstract and Poster, presented during one of the Poster Scessions**

★★★★ **Abstract and Poster, presented during one of the Poster Scessions and Awarded during the Closing Ceremony**

1. EXPLOITATION OF RENEWABLE RESOURCES

Chiral photoelectrodes for efficient generation of Hydrogen through photocatalytic water splitting
Rufaro KAWONDERA, Wilbert MTANGI, Stephen NYONI, and Gift MEHLANA

Silicon doped Microporous Carbon Derived from Natural Fibers for Efficient Supercapacitor Device
Doha M. Sayed, Mohamed S. El-Deab, and Nageh K. Allam

Multiple synergistic effects of Zr-alloying on the phase stability and photostability of black niobium oxide nanotubes as efficient photoelectrodes for solar hydrogen production
Kholoud E. Salem, Abdelrahman M. Mokhtar, and Nageh K. Allam

Controlled Fabrication of Mesoporous Electrodes with Unprecedented Stability for Water Capacitive Deionization Under Harsh Conditions in Large Size Cells
Manar M. Taha, Soha E. Anwar, Mohamed Ramadan, Hazem M. Al-Bulqini, Muhammed S., and Nageh K. Allam

Bio-inspired of Fe doped $BiVO_4$ Nanoparticles via *Hyphaene thebaica* natural extract and their photocatalytic MB degradation properties
Hamza MOHAMED, Alain GIBAUD, and Malik MAAZA

Synthesis of aminated magnetite nanoparticles and their interaction with biomembrane models
Santiago D. SALAS, Nancy FERREYRA, and Raquel V. VICO

Holistic synthesis of low-cost Fe-based MOFs using unconventional metal feedstock and PET-derived organic linkers
Nqobile Mthembu, Henrietta W. Langmi, and Nicholas M. Musyoka

Catalytic hydrogenation of CO_2 by n-triphosphine metal complexes in bicyclic phosphonium ionic liquids
Bongiwe. B. GAMBU, Banothile. C. E. MAKHUBELA, and Chris. MAUMELA

Analytical and biological characterization of the lipophilic extract profile of chaga (Inonotus obliquss)
Karina Upska, Linards Klavins, Inga Sile, Vizma Nikolajeva, Leena Faven, Eveliina Isosaari, and Maris Klavins

Silymarin extraction for *Silybum marinuim* seeds using pressurized liquid extraction as a green and efficient technology
Norelhouda ABDERREZAG, Zully Jimena SUAREZ-MONTENEGRO, Wahida LOUAER, Abdeslam-Hassen MENIAI, Elena IBAÑEZ , and José A. MENDIOLA

Production and formulation of a biofertilizer to promote potato growth
Imtinen SGHAIER, Hanen CHERIF, Wafa HASSEN, Ameur CHERIF, and Mohamed NEIFAR

Lipase immobilization on pristine and modified carbon nanotubes in order to obtain an efficient and environmentally friendly biocatalysts
Iryna Sulym, Jakub Zdarta, Filip Ciesielczyk, and Teofil Jesionowski

Modified Activation Process for Supercapacitor Electrode Materials from African Maize Cob
Moses KIGOZI, Ravi KALI, Abdulhakeem BELLO, Balaji PADYA, Godwin Mong KALU-UKA, John WASSWA, Pawan Kumar JAIN, Peter Azikiwe ONWUALU, and Nelson Yaw DZADE

Greener biomass-based composite for excellent green extraction tools
Nur Husna Zainal Abidin, Wan Nazihah Wan Ibrahim, Norsuhaila Mohamad Hanapi, and Nursyamsila Mat Hadzir

New lignan derivative from *Pachypodanthium barteri* (Benth). (Annonaceae)
Pascal D. Douanla, Thierry K. Wafo, Sammer Yousuf, Turibio Kuiate Tabopda, Saira Bano, Alembert T. Tchinda, Iqbal Choudhary, and Marguerite Hortence K. Tchuendem

Regiodivergent Isosorbide Acylation by Oxidative NHC-Catalysis in Batch and Continuous-Flow
Daniele RAGNO, Costanza LEONARDI, Graziano DI CARMINE, Arianna BRANDOLESE, Francesca DESTASO, and Alessandro MASSI

Valorisation of sludge biomass from civil wastewater
Reshma BABU, Gustavo CAPANNELLI, and Antonio COMITÉ

Polyhydroxybutyrate as a sustainable platform for the production of chemicals and bio-polymers
Adriano PARODI, Chiara SAMORI, and Paola GALLETTI

Green amination strategies for the production of biobased building-blocks
Denise CAVUOTO, Antonella GERVASINI, Federica ZACCHERIA, and Nicoletta RAVASIO

Comparison of rapid calibration models to predict the composition of biomass based on FT-NIR, FT-IR and solid-state NMR
Kristoffer M. HERDLEVÆR and Tanja BARTH

Carboxymethyl chitosan films – properties
Marta SZULC and Katarzyna LEWANDOWSKA

Ecological dyeing of natural fabrics with renewable raw materials-plant derived colorants
Patrycja BRUDZYŃSKA and Alina SIONKOWSKA

Outline of a Process for the Hydrothermal Liquefaction of a Tannery Sludge for Biofuel Production
Francesca DI LAURO, Marco BALSAMO, Roberto SOLIMENE, Piero SALATINO, and Fabio MONTAGNARO

Recycling Agricultural Wastes and By-products in Organic Farming
Samar Mousa

Bio-based and eco-friendly products as efficient alternatives to commercial biocides for the production of sustainable sol-gel based antifouling coatings
Angela CASTELLANO, Silvia SFAMENI, and Maria Rosaria PLUTINO

Adding value to pulp industry waste: Bio-based thermosetting epoxy resins using Kraft lignin
Christina PAPPA and Konstantinos S. TRIANTAFYLLIDIS

Plant metabolites as stimulants and/or inhibitors of parasitic plant seed germination
Gabriele Soriano, Alessio Cimmino, Mónica Fernández-Aparicio, Marco Masi, and Antonio Evidente[a]

2. NEW REACTION PATHWAYS

Efficient degradation of Carbamazepine (CBZ) from waste water using combined effect of immobilized laccase and ultrasound
Mayur LADOLE*, Vrushali VARUDE, and Aniruddha PANDIT

Understanding the mechanism of Ir(III) catalyzed CO_2 hydrogenation in water
Edward OCANSEY, James DARKWA, and Banothile MAKHUBELA

Synthesis, crystal structures and photocatalytic study of coordination polymers constructed from tetracarboxylate ligand
Adetola OLADIPO, Adedibu TELLA, Victoria OLAYEMI, Guy CLARKSON, and Richard WALTON

Metal-free, highly soluble, fully aromatic fluorinated ladder polymer
Manuel Rodríguez-Molina and Mikhail G. Zolotukhin

Metal-free, highly soluble, fully aromatic fluorinated ladder polymer
Manuel Rodríguez-Molina and Mikhail G. Zolotukhin

Visible light to generate excited anion radicals of Naphthalene Diimides
Sofia CABY and Javier BARDAGI

Biocatalytic approach for enantiomeric resolution of benzothiazolines and benzoimidazolines using MAO enzyme
Valentina VILLAMIL, Cesar IGLESIAS, Cecilia SAIZ, Sonia RODRIGUEZ, and Graciela MAHLER

Green synthesis of ZnO coated hybrid biochar for the synchronous removal of Ciprofloxacin and Tetracycline in Wastewater
Abisola O. Egbedina, Kayode O. Adebowale, Bamidele I. Olu-Owolabi, Emmanuel I. Unuabonah, Morenike O. Adesina

Condensation Reactions of Methyl Derivatives of Quinoxaline and Quinoxaline-1,4-dioxide with Aromatic Dialdehyde
Mohamad ALKHUDARI, Adnan ATFEH, and Rushdi MADWAR

Facile *in situ* formation of luminescent cellulose paper using a novel solvent-based approach
Stephanie A. FRASER, Michael N. PILLAY, and Werner E. VAN ZYL

Efficiency improvements of CO_2 utilization: the case of styrene carbonate synthesis in microdroplets conditions
Caterina ROVEGNO, Daniele URBANI, Eleonora POLO, Alessandro MASSI, and Paolo DAMBRUOSO

Preparation of single-atom catalysis based on carbon nitride materials

Thiago de Melo Lima

Hydrothermal Conversion of Digested Waste Water Sludge from Biogas Plant to Valuable Components

Stian H. HEGDAHL, Camilla LØHRE, and Tanja BARTH

Reactive Deep Eutectic Solvents (RDESs): a new tool for Phospholipase D-catalyzed preparation of polar head modified phospholipids

Letizia Rossato, Chiara Allegretti, Francesco Gatti, Stefano Marzorati, Stefano Serra, Alberto Strini, and Paola D'Arrigo

Selective oxidative cleavage of C-C double bonds by hydrogen peroxide

Monika HORVAT and Jernej ISKRA

Pillararene-Based PES blended polymers: Design, Preparation and Sustainable Applications

Anna NOTTI, Giulia RANDO, and Maria Rosaria PLUTINO

Design and development of anti-fouling eco-friendly coatings for marine applications

S. SFAMENI, A. CASTELLANO, S. CAPPELLO, A.VISCO, and M. R. PLUTINO

Development of hybrid geopolymeric-based materials suitable for building sector

Fausta GIACOBELLO, Ileana IELO, Maurilio GALLETTA, and Maria Rosaria PLUTINO

Picolinium-based Eutectic Systems (ESs) in the Lubrication of Silicon Surfaces

Mariana DONATO, Hermínio DIOGO, Luís SANTOS, Rogério COLAÇO, Luís C. BRANCO, and Benilde SARAMAGO

Synthesis and Characterization of Novel Ionic Liquid Crystals-based on Substituted Pyridinium Cations

Andreia F. M. SANTOS, Maria H. GODINHO, Madalena DIONÍSIO, J.L. FIGUEIRINHAS, and Luis C. BRANCO

Isocyanide-bases One-Pot Synthesis of Thiocarbamates

Kevin A. Waibel, Dennis Barther, Triantafillia Malliaridou, Dafni Moatsou, and Michael A.R. Meier

Development of a low environmental impact couple of solvent and catalyst for Nenitzescu reaction

Andrea Beccu, Giuseppe Satta, Ugo Gavino Azzena, Luisa Pisano, and Massimo Carraro

Levulinic Acid Hydrogenation to γ-valerolactone over Single Ru Atoms on TiO_2@Nitrogen Doped Carbon Support

Kaili Zhang, Qinglei Meng, Haihong Wu, Tongying Yuan, Shitao Han, Jianxin Zhai, Bingxiao Zheng, Caiyun Xu, Wei Wu, Mingyuan He, and Buxing Han

Base and Acid Free copper catalysed C-H ammination

Valentina MARUZZO, Filippo PETTAZZI, Katia MARTINA, and Giancarlo CRAVOTTO

Flash Vacuum Pyrolysis as a Green, Solvent–Free Technology

Michaela WERNIK, Dragan ZLATKOVIĆ, Gellért SIPOS, Ferenc DARVAS, Doris DALLINGER, and C. Oliver KAPPE

3. ENERGY SAVING

Design of Efficient, Stable and Lead Free Perovskite Solar Cells
Paul CHAWAGARIRA, Wilbert MTANGI, and Engelbert KAPUYA

Co–Cu Bimetallic Metal Organic Framework Catalyst Outperforms the Pt/C Benchmark for Oxygen Reduction
Mohamed Fathi Sanad, Alain R. Puente Santiago, Sarah A. Tolba, Md Ariful Ahsan, Olivia Fernandez-Delgado, Mina Shawky Adly, Elhussein M. Hashem, Mohamed Mahrous Abodouh, M. Samy El-Shall, Sreeprasad T. Sreenivasan, Nageh K. Allam, and Luis Echegoyen

Photocatalytic H_2 production from H_2S decomposition
Maali-Amel MERSEL, Lajos FODOR, and Ottó HORVATH

Next generation of green OPV cells based on water-soluble photo-active material
Debora QUADRETTI, Massimiliano LANZI, Martina MARINELLI, and Elisabetta SALATELLI

Interaction of [NiFe] hydrogenases on a graphite electrode
Manuel Ruiz and Guido Raos

4. FOOD SAFETY

Photocatalytic degradation of fungicide difenoconazole via photo-Fenton process using α-Fe_2O_3
Hajar LAMKHANTER, Sana FRINDY, Yuri PARK, Mika SILLANPÄÄ, and Hafida MOUNTACER

Development of green methodologies in the chemical research of by-products and wastes from coffee crops and coffee processing
Mariana Rodrigues Da Silva, Felipe Sanchez Bragagnolo, Renato Lajarim Carneiro, José Antonio Aquino Ribeiro, Clenilson Martins, Rebecca E. Jelley, Bruno Fedrizzi, Cameron Weber, and Cristiano Soleo Funari

A green approach to valorize soy agro by-products
Felipe Sanchez BRAGAGNOLO, Bárbara SOCAS-RODRÍGUEZ, Jose A. MENDIOLA, Cristiano Soleo FUNARI, and Elena IBÁÑEZ

Development of a novel UHPLC-MS/MS method for the determination of ochratoxin A in tea: Greenness assessment
Mariel CINA and Soledad CERUTTI

Improving the performance of thin film nanocomposite membrane used for water treatment and desalination
Mohammed KADHOM, Mustafa ALFURAIJI, and Emad YOUSIF

Sugar-based surfactants: chemoenzymatic synthesis and interfacial properties evaluation
Sara SANGIORGIO, Riccardo SEMPROLI, Teodora BAVARO, Giuseppe CAPPELLETTI, Giorgio MARRUBINI, Marco RABUFFETTI, Sara NASSERIAN, Marina S. ROBESCU, Daniela UBIALI, and Giovanna SPERANZA

5. CLIMATE CHANGE DAMAGES MITIGATION

Adsorptive removal of methylene blue dye from aqueous solution using biodegradable superabsorbent polymer hydrogel and its composites
Syed Sikandar SHAH and Antonio Carlos Silva Costa TEIXEIRA

Microwave-driven hydrothermal synthesis of α-Fe_2O_3 nanorings as CeO_2 catalyst support for CO_2 conversion
Aryane A. MARCINIAK, Evelyn C.S. SANTOS, Odivaldo C. ALVES, Flavio GARCIA, and Claudio J.A. MOTA

Pb-Zn mine wastes based geopolymers: Microstructure, technological and heavy metals adsorption properties
Jihene NOUAIRI, Slavka ANDREJKOVIČOVÁ, Fernando ROCHA, and Hedi BEN MANSOUR

Photocatalytic removal of toxic metal ions from water using functionalized g-C_3N_4
Timothy O. AJIBOYE, Alex T. KUVAREGA, and Damian C. ONWUDIWE

Anion Exchanger on the base Polyvinylchloride for Efficient Removal Hexavalent Chromium Ions in Aqueous Media
Davronbek BEKCHANOV, Mukhtar MUKHAMEDIEV, and Gulbakhor BABOJONOVA

Development of new homogenous catalysts for CO_2 reduction to formates
Asanda C. Matsheku, Chris Maumela, and Banothile C.E. Makhubela

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Fully renewable NIPUs *via* thiol-ene polymerization
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1. EXPLOITATION OF RENEWABLE RESOURCES

Chiral photoelectrodes for efficient generation of Hydrogen through photocatalytic water splitting

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The quest for cleaner and renewable energy sources has led to increased research into photoelectrocatalytic water-splitting which mimics natural photosynthesis by producing hydrogen using solar energy in the presence of a photoelectrocatalyst. Hydrogen is considered an ideal energy source for the future as it does not contain carbon and produces benign combustion by-products. Although considerable research into photoelectrocatalytic water-splitting has been carried out, the current methods are not efficient due to high Oxygen Evolution Barrier, high overpotential and formation of hydrogen peroxide which also affects the stability of the photoelectrodes, etc; photoelectrocatalytic production of hydrogen remains in the future. It has been suggested theoretically that the over-potential results from spin restriction in the oxygen production. DFT calculations as well as experimental observations have revealed that the over-potential for water splitting is greatly reduced when magnetic materials are used [1-4] Experimental observations have also indicated that the formation of hydrogen peroxide in an electrochemical cell is a competing process to the formation of the triplet oxygen molecule. It has also been demonstrated experimentally that hydrogen peroxide formation is suppressed in electrochemical cells where electron spin is preserved [5-7]. A concomitant reduction of the over-potential was achieved in cells where the electron spin was preserved [8]. These observations suggest that spin alignment is essential for lowering the over-potential and increasing the efficiency of water splitting. In this paper we highlight the importance of spin on water splitting based on results from theoretical studies and experimental observations.

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Silicon doped Microporous Carbon Derived from Natural Fibers for Efficient Supercapacitor Device

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The development of sustainable and renewable energy storage systems is a promising approach towards steady and reliable energy supply. In this study, cellulosic natural fibers were used as a precursor to produce microporous carbon (m-C) that contains embedded silicon oxide. The m-C exhibits a fairly high BET surface area (2000m^2/g) and a 3D-microporous structure with small mesopores. The symmetric m-C//m-C supercapacitor device tested in 1.0 M NaCl aqueous electrolyte showed fairly high specific capacitances of 201 F/g at 5 mV/s. The device exhibits a stable performance across a potential window of 1.8 V with ultra- high energy and power densities of 51.4 Wh/kg at 4.5 kW/kg and 16.95 Wh/kg at 18 kW/kg. The device showed extraordinary increasing capacitive behavior upon cycling at 10 A/g for over 25,0000 cycles. The exceptional device performance could be ascribed to the electrochemical graphitization during long-term cycling together with the enhanced wettability as confirmed via Raman, FTIR, XPS, XRD, and contact angle measurements.

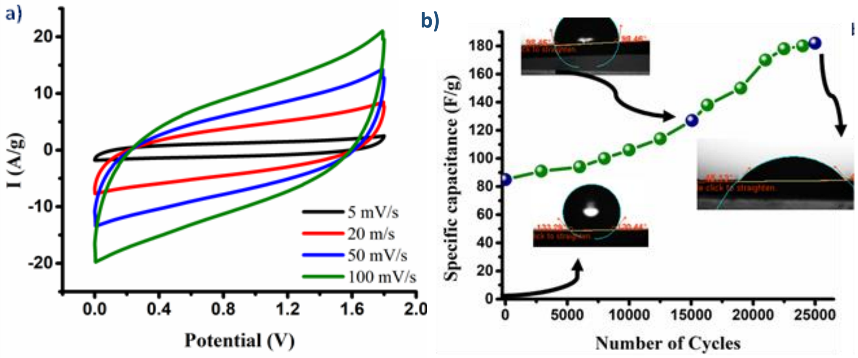

Figure 1. (a) CVs of m-C//m-C supercapacitor device tested in 1.0 M NaCl aqueous electrolyte at various potential scan rate. (b) Cyclic stability of the symmetric device with insets indicating the contact angle measurements.

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Multiple synergistic effects of Zr-alloying on the phase stability and photostability of black niobium oxide nanotubes as efficient photoelectrodes for solar hydrogen production

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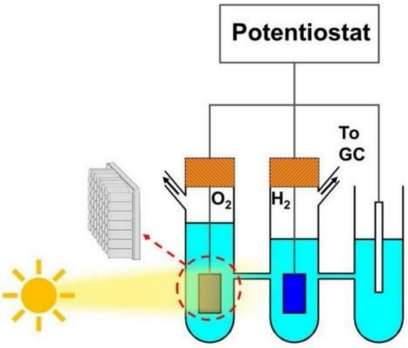
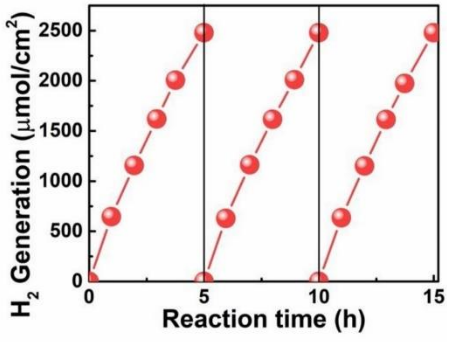
Niobium oxides exist in a plethora of metastable, stoichiometric, nonstoichiometric, and mixed phases, rendering the Nb-O systems very complicated and hard to study. These structures significantly differ in their catalytic activity, electrical conductivity, and photoresponse. Herein, we demonstrate the ability to selectively fabricate pure T-Nb_2O_5 *via* the addition of small amount of Zr as a phase stabilizer. Moreover, we were able to tune the photoactivity of the material *via* hydrogen annealing. The photoactivity and stability of the fabricated black Zr-doped Nb_2O_5 nanotubes were correlated with the nature of induced defects upon hydrogen annealing and Zr doping. The H_2-treated nanotubes showed extraordinary and remarkable stability and photoactivity upon their use for solar water splitting. This was accompanied by a noticeable reduction in the bandgap energy from 3.23 eV to 2.5 eV, which is mainly correlated with the introduced oxygen vacancies within the lattice with a remarkable conductivity. Most importantly, the black-defective nanotubes exhibited a photocatalytic activity that is ~ 65 times that of the air-annealed counterparts. The optimized photoanodes attained a hydrogen production rate of ~ 496 $\mu mol\ h^{-1}\ cm^{-2}$ in 1 M KOH, revealing increased charge carriers transport and separation. The Mott-Schottky and valence band XPS analyses confirmed the increased charge carriers' concentration and the appropriate band positions of the fabricated black nanotubes relative to the redox potentials of the water.





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Controlled Fabrication of Mesoporous Electrodes with Unprecedented Stability for Water Capacitive Deionization Under Harsh Conditions in Large Size Cells

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Capacitive deionization (CDI) is a feasible low-cost desalination technique for low-to-medium (brackish) salinity water. However, cycling stability and regeneration of the CDI electrodes are the bottlenecks hindering the practical application of the technology on large scale. Oxidation of the electrodes during the sequential adsorption-desorption processes is one of the most challenging problems hindering their long-term cycling performance. Herein, we demonstrated the ability to design and fabricate exceptionally stable CDI electrodes via a one-pot pyrolysis protocol. The optimized pyrolysis of nitrogen-carbon precursors at different temperatures enabled the fabrication of carbon materials with a controlled amount nitrogen dopant (NDCs) with exceptional cycling stability. The NDCs showed high specific capacitance and dual meso/microporous structures with high salt adsorption capacity (SAC), reaching 26.5 mg. g-1 in a single-pass desalination mode. Moreover, the electrodes exhibited exceptional desalination stability performance over 150 successive charging/discharging cycles with 100 and 90 % retention in aerated and deaerated solutions respectively, under harsh 1.4 V as the charging voltage. The potential of zero charge (PZC) was determined for the tested NDC electrodes to elucidate their oxidation resistance (EOR). The electrodes exhibited a minimal shift in potential after the entire desalination stability tests, revealing minor electrode oxidation. The performance of our NDC-electrodes was compared against that of the commercially available activated carbon (AC) under the same experimental conditions, with the latter showing a server decrease in the SAC retention within the first few cycles

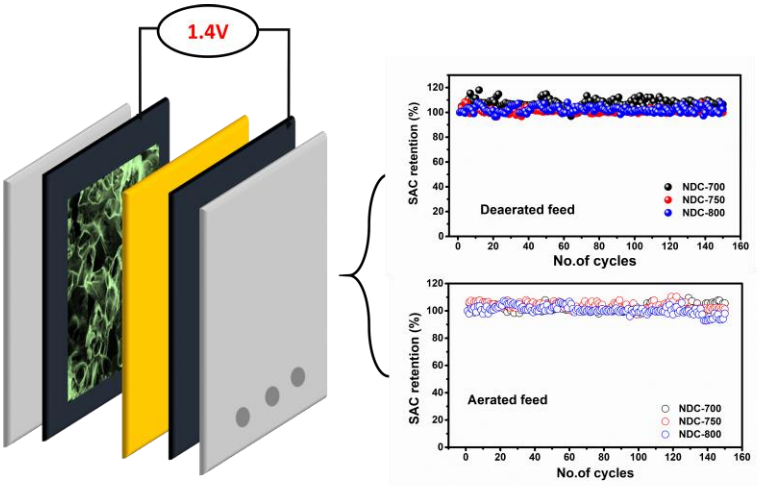

Figure 1. schematic diagram of the long term stability of the capacitive deionization process revealing a successful

Bio-inspired of Fe doped $BiVO_4$ Nanoparticles via *Hyphaene thebaica* natural extract and their photocatalytic MB degradation properties.

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This contribution reports for the 1st time on the bio-synthesis of Fe doped BiVO4 nanorods using extracts of Hyphaene thebaica as an effective chelating and capping agent. Their surface & interface properties of such Fe: $BiVO_4$ nanocrystals were investigated via several complementary techniques including X-Ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (TEM), & Selected Area Electron Diffraction (SAED),as well as Electron Dispersion X-ray Spectroscopy (EDS), UV-VIS diffuse reflectance spectroscopy (DRS), Fluorescence, and Raman Spectroscopy. The study confirmed the single phase crystalline BiVO4 phase with Fe as an interstitial dopant. The major effect of the Fe doping was correlated to the optical bandgap tunability. Th annealed Fe:BiVO4 1-D nano-crystals were found to exhibit a significanton photocatalytic degradation of methylene blue (MB) in the Visible spectral range.

Synthesis of aminated magnetite nanoparticles and their interaction with biomembrane models

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The widespread applications of magnetic nanoparticles (MNP) in i.e. biomedicine, sensing, and environmental remediation have increased in the last years. However, the dissemination of these novel materials in the environment and their potential toxicity have become an issue of major concern. The first natural barrier that NP find when they interact with living cells is the cellular membrane. The study of the effects of NP in organisms and cells can be complex, though, due to difficulties in the control of several variables. In this sense, the application of simplified and controlled biomembrane models, such as Langmuir monolayers, can be accurate to elucidate the molecular and supramolecular mechanisms that modulate NP-biointerface interaction and determine the mechanisms of toxicity. In previous work, we have synthesized different types on NP with a wide range of capping agents, and we assessed their interactions con biomembrane models using Langmuir monolayers comprising different types of lipids. [1][2]

In this work we show the synthesis of magnetite (Fe_3O_4) MNP capped with an aryl diazonium salt (MNP@Ar-NH2) [3] (Figure 1), followed by cross-linking with glutaraldehyde (GA) (MNP@GA), and then, a Schiff base formation with branched polyethylenimine (PEI) to amplify amine groups on the surface (MNP@GA@PEI) [4]. TEM, XRD, TGA, zeta potential and hydrodynamic radii vs pH, FT-IR, and amine quantification confirm the presence of the new functional groups after each capping step. Furthermore, we will assess the effect of MNP@GA@PEI concentration and charge on the interaction with a dimyristoylphosphatidylcholine (DMPC) monolayer on an aqueous subphase as a biomembrane model using a Langmuir minitrough.

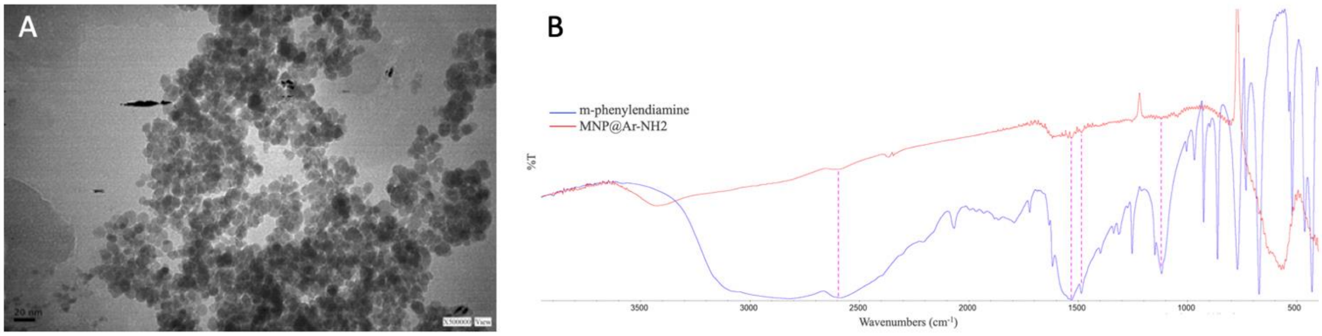

Figure 1. (A) TEM image of MNP@Ar-NH2 and (B) FT-IR spectra of m-phenylendiamine and MNP@Ar-NH2.

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Holistic synthesis of low-cost Fe-based MOFs using unconventional metal feedstock and PET-derived organic linkers

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Due to the over-reliance on fossil fuels, their depletion and emission of harmful gasses has raised a lot of concerns across the globe and as a result, alternative energy resources have been explored. Biogas, a renewable energy resource, has high CH_4 content and can replace fossil fuel. However, the use of raw biogas is limited due to impurities (such as CO_2, H_2S, $H_2O_{(v)}$, etc.), which inhibits its high-value application. Since CO_2 is the major unwanted constituent in the biogas (~30-40%) that decreases its calorific value, there is a need to separate it to obtain biomethane (biogas upgrading).[1] Of the several methods employed in biogas upgrading, the use of the Pressure Swing Adsorption (PSA) technology has proven to be the most attractive option. The performance and efficiency of PSA is often dependent on the choice of the adsorbent material.[2] Among many other sorbent materials, Metal-organic frameworks (MOFs) have been shown to exhibit superior performance due to their unique properties such as large surface areas and high pore volumes and tuneable pore structures.[3] However, because their starting feedstock materials are expensive, only a few MOFs types have been produced at an industrial scale. This project focuses on the use of waste materials such as polyethylene terephthalate (PET), as a source of the organic linker and acid mine drainage (AMD) as a feedstock for metal ions. The use of these waste feedstocks could reduce MOFs' production costs whilst eliminating their disposal in landfills and inherent harmful environmental effects.

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Catalytic hydrogenation of CO_2 by n-triphosphine metal complexes in bicyclic phosphonium ionic liquids

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CO_2 hydrogenation process can be made greener by utilizing sustainable solvents called ionic liquids as reaction media which dissolve CO_2 better than conventional organic solvents [1] Furthermore, advantageous of low-vapor pressure, mechanical stable, non-flammable, and reusable [2]. In addition, phosphonium ionic liquids have increase stability in comparison to imidazolium.[3] The evolution of existing fossil-based to bio-based ionic liquids is due to the limitations of slight toxicity. These advantages have prompted us to design novel phosphonium bio-based ionic liquids from bio-based material called Limonene which is derived from terpenes.

In addition, well defined highly stable triphosphine analogue catalysts with excellent donor - acceptor abilities [4] which show promising results methanol and ethylene glycol [5] and now having nitrogen moiety will be coordinated to first row transition metals (Mn, Fe, Co, and Ni), in efforts to develop active and cost-effective CO_2 hydrogenation catalysts.

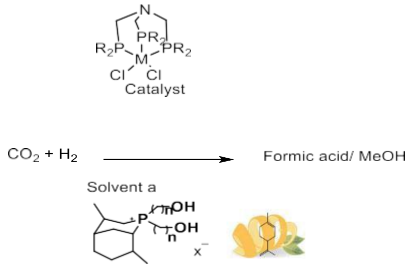

Figure 1: CO_2 hydrogenation using bio-based (Limonene) ionic liquids.

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Analytical and biological characterization of the lipophilic extract profile of chaga (Inonotus obliquss)

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Chaga (*Inonotus obliquus*) (Fr.) Pilát is a black perennial fungus of the *Hymenochaetaceae* family that parasites on adult birch trunks as well as on other types of broadleaf tree species - alder, mountain ash. *Inonotus obliquus* produces a wide range of bioactive metabolites, including triterpenoids, sterols, polysaccharides, polyphenols. These compounds have antioxidant, antitumor, and antiviral activity and the ability to increase immunity to pathogenic microbial infections.

The aim of the study is to obtain the maximum high yield of extracts with anti-cancer activity. This would allow the development of industrially based components based on green raw material that can participate in the correction and prevention of pathological disorders. Large-scale extraction can be accomplished by environmentally friendly supercritical fluid extraction (CO_2). Chaga lipophilic compounds were isolated by different extraction methods (Soxhlet, ultra-sonic, accelerated solvent and super-fluid extractions) using different non-polar solvents and were compared. Chaga's lipid extract was fractionated and the effect of the obtained fractions on pathogenic microorganisms and A-549, MCF7, B16-F10, CaCo-2 cancer cell lines was tested. The antimicrobial properties of the obtained extracts were characterized by agar diffusion test and anticancer activity by MTT (colorimetric assay for assessing cell metabolic activity) test.

Silymarin extraction for *Silybum marinuim* seeds using pressurized liquid extraction as a green and efficient technology

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It well-known that Silymarin complex (a mixture obtained from the seeds of milk thistle, *Silybum marinuim*) display a wide range of biological activities, including antioxidant, anti-inflammatory, cytoprotective and neuroprotective properties [1]. The classic method to isolate the Silymarin, consist of two steps, one to remove the lipids using hexane for 5 to 7 hours, followed by an organic solvent extraction. However, this process has many drawbacks such as long operation time, large solvent volume, inadequacy for thermolabile compounds. To overcome this, the pressurized liquid extraction (PLE) of Silymarin, in one-step, was carried out using a mixture of green solvents (ethanol/water). The effects of percentage of ethanol in the solvent mixture (0, 20, 50, 80, and 100 %) and temperature (75, 125, 175 °C) on the total recovery, total phenolic content (TPC) and total flavonoid content (TFC) are examined. The maximum extracted yield obtained was 49.20% at 175C °C using 80/20 ethanol/water. The chemical analysis by UHPLC-ESI-MS/MS has been developed for quantification of six flavonolignans present in Silymarin. Furthermore, different bioactivities including enzymatic (acetylcholinesterase (AChE) and lipoxygenase (LOX)) as well as antioxidant (reactive nitrogen species (RNS)) activity tests have been applied in vitro.

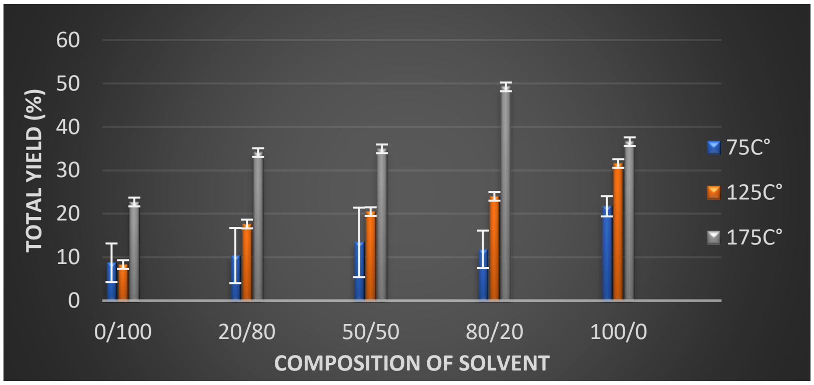

Figure 1. Total yield of pressurized liquid etraction of Silybuim marinum using ethanol/water at different temperature.

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Production and formulation of a biofertilizer to promote potato growth

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A part of our study has investigated PGPR traits focusing on phosphorus solubilization ability of a bacteria collection. *Pseudomonas rhizophila* S211, isolated from a pesticide contaminated artichoke field has been shown a wide spectrum of PGP traits. The in vitro tests revealed that S211 was able to grow under high salinity (10% NaCl) and alkalinity (pH 9), fix nitrogen, synthetize auxine, HCN, ammonia, pyoverdine-siderophores, produce exopolysaccharides and organic acids and solubilize rock phosphate. S211 showed a solubilization index equal to 1 on NBRIP agar medium and a decrease in pH from 6.7 to 4.2 on NBRIP liquid medium. Morever, the genome sequence analysis confirmed the presence of genes involved in plant growth promoting and phosphorus solubilization activities such as the synthesis of auxin, pyroverdine, exopolysaccharide, ACC deaminase, putative dioxygenases, phosphatases and glucose dehydrogenases. furthemore, S211 has been shown an ability to promote potato growth under green house and also in field. These results prove that the biofertilizer formed by the bacterium *Pseudomonas rhizophila* S211 could substitute chemical intrants and promote green chemistry and sustainable agriculture [1-2].

Acknowledgements

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Lipase immobilization on pristine and modified carbon nanotubes in order to obtain an efficient and environmentally friendly biocatalysts

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Nanobiocatalysis, which refers to the application of enzymes immobilized on nanomaterials, is a rapidly growing research field [1, 2]. Various nanomaterials, such as nano-SiO_2, nano-TiO_2, nanogold, carbon nanotubes, and graphene, have been explored as support materials [3,4].

In the current work, for the first time, the methodology to design and characterize an alternative, highly stable and active nanobiocatalyst based on *Candida antarctica* lipase B (CALB) immobilized onto pristine and poly(dimethylsiloxane) (PDMS) modified multi-walled carbon nanotubes (MWCNTs) is presented and discussed. The idea is to combine the textural properties as well functionality of PDMS modified MWCNTs with lipase activity and to obtain novel type of biocatalyst dedicated for biotechnological applications.

The MWCNTs/PDMS nanocomposites, containing 40 wt. % of the polymer with two molecular weights (PDMS-100 and PDMS-12500 with $M_w \approx 3410$ and 39500 g/mol, respectively), were successfully synthesized via adsorption modification. Effect of PDMS chains length on the textural/structural properties of the produced materials was studied by means of nitrogen adsorption–desorption technique, Raman spectroscopy, scanning electron microscopy and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Pristine MWCNTs (P-MWCNTs) and MWCNTs/PDMS nanocomposites were tested as supports for lipase immobilization. Successful deposition of the enzyme onto surface of P-MWCNTs and MWCNTs/PDMS nanocomposite materials was confirmed mainly using ATR-FTIR spectroscopy. Enzyme loaded onto P-MWCNTs and MWCNTs/PDMS nanocomposites showed significantly higher relative activity over wider pH and temperature range as compared to free counterpart. Moreover, significant improvement of thermal stability and enzyme half-life of the lipase after immobilization was observed. It was confirmed that after immobilization external backbone for the enzyme structure is provided due the formation of stable enzyme-support interactions, which stabilize enzyme structure and protect against biocatalysts denaturation at harsh reaction conditions. This fact suggests wide application potential of designed novel type of biocatalytic systems in various technological/biotechnological applications.

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Modified Activation Process for Supercapacitor Electrode Materials from African Maize Cob

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In this work, African maize cobs (AMC) were used as a rich biomass precursor to synthesize carbon material through a chemical activation process for application in electrochemical energy storage devices. The carbonization and activation were carried out with concentrated Sulphuric acid at three different temperatures of 600, 700 and 800 °C, respectively. The activated carbon exhibited excellent microporous and mesoporous structure with a specific surface area that ranges between 30 and 254 m2·g−1 as measured by BET analysis. The morphology and structure of the produced materials are analyzed through Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Boehm titration, X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy. X-ray photoelectron spectroscopy indicates that a considerable amount of oxygen is present in the materials. The functional groups in the activated carbon enhanced the electrochemical performance and improved the material's double-layer capacitance. The carbonized composite activated at 700 °C exhibited excellent capacitance of 456 F g−1 at a specific current of 0.25 A g−1 in 6 M KOH electrolyte and showed excellent stability after 10,000 cycles. Besides being a low cost, the produced materials offer good stability and electrochemical properties, making them suitable for supercapacitor applications.

Greener biomass-based composite for excellent green extraction tools

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Conventional sample pre-treatment methods such as liquid-liquid extraction and solid phase extraction are subjected to criticism from a green chemistry perspective due to excessive consumption of hazardous solvents and materials in multi-steps process [1]. In the past several decades, the development of miniature sample preparation techniques has received a lot of attention as a key to meet green analytical chemistry principles. Miniaturization technique portrays minute use of harmful organic solvents, automating, integrated online with analytical instruments, and lowering energy consumption [2]. While the underlying idea of miniaturization extraction process bring in the green character, exploring the development of the sorbent material nature is also crucial for improving the greenness of an analytical method. Recently, the repurposing of agro-industrial biomass has led to the use of new low-cost adsorbents derived from renewable sources. So far, researchers have attempted to capitalize on these various parts of a plant or agro-industrial biomass in order to manufacture low-cost adsorbents in accordance with the Malaysian government's wave of "Zero Waste Initiatives" [3]. Malaysia's palm oil production is increasing drastically every year due to its high demand in the global market, and it tends to produce more biomass. Thus, it is necessary to exploit the massive amount of oil palm biomass generated for other value-added products [4]. The aim of this research is to exploit the massive abundance of Malaysia's oil palm biomass for valuable products. Scope of research focusing on investigation production of adsorbent from different oil palm part such as activated carbon, char, ash, silica and nanocellulose and serve as new sorbent materials for trace analysis of organic and inorganic environmental pollutants. These sorbents offer an excellent adsorption behaviour due to their nanoparticle sizes, high surface area and large sorption capacity which comparable with the commercialised sorbent. The outcome of this research will lead to the exploration of more advanced nanomaterials for environmental application where it comply with the objectives of Green Chemistry and Susistanable Development Goals (SDGs), where the research community has to reorient its activities in line with industry needs to convert waste to wealth and minimizes the negative impacts on human activities.

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New lignan derivative from *Pachypodanthium barteri* (Benth). (Annonaceae)

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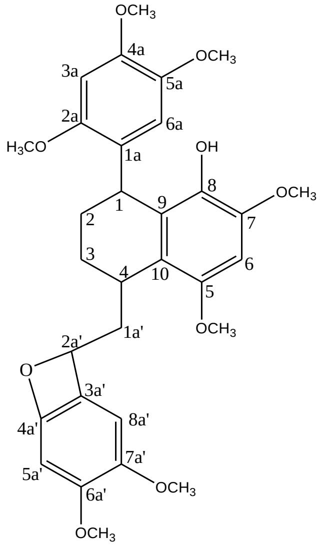
Chemical investigation of the fruits of *Pachypodanthium barteri* resulted in the isolation of one new lignan, designated pachypobarter (1), along with six known compounds compounds identified as Pachypostaudin A (**2**) and B (**3**) Pellucidin A (**4**), Pachypodol (**5**) [**1,2**] and β-Amyrin glucoside (**6**) [**3**]. The structures of the new compound was elucidated on the basis of extensive spectroscopic analyses including, IR, UV, 1D and 2D – NMR as well as HRMS data. The isolated compounds were evaluated for their in vitro leishmanicidal activity against L. major (DESTO) promastigotes, anticancer activity on PC3 (prostate cancer) cell line and *in vitro* cytotoxicity on MCF-7 cell lines.

Key words: *Annonaceae, Pachypodanthium barteri, lignan, leishmanicidal activity, anticancer activity, cytotoxicity*



pachypobarter

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Regiodivergent Isosorbide Acylation by Oxidative NHC-Catalysis in Batch and Continuous-Flow

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With increasing interest in lignocellulosic biomass waste valorization [1], isosorbide (**IS**) has emerged as an attractive renewable feedstock for the production of bio-based platform chemicals. **IS** is a chiral, rigid, non-toxic diol derived from glucose, which displays a bi-heterocyclic V-shaped backbone made of two fused furan units bearing two secondary non-equivalent hydroxyl groups at C5 and C2 positions in endo and exo configurations, respectively [2]. The regioselective functionalization of the 2- and 5-hydroxyl groups is a thriving strategy to obtain high-added valued **IS**-based products with different chemical, biological, and physical properties.

In this context we describe an unprecedent N-heterocyclic carbene (NHC)-organocatalyzed strategy under oxidative conditions for the fully regiodivergent synthesis of endo and exo monoacyl-isosorbides (MAIs), using aldehydes as mild acylating agents, including the biorefinery products furfural and 5-hydroxymethyl furfural. Additionally, our *exo*-selective strategy was successfully transferred into heterogeneous phase and applied to continuous-flow catalysis, through the fabrication and long-term operation of the corresponding packed-bed mesoreactor to produce the 2-benzoyl-**IS** (**IS**-5MN) which is the key intermediate in the synthesis of the commercial vasodilator isosorbide-5-mononitrate.

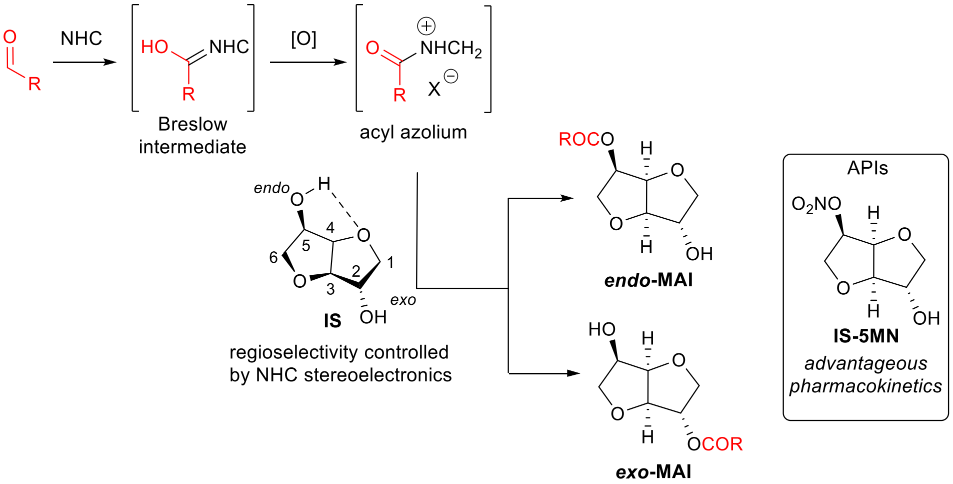

Figure 1. N-heterocyclic carbene (NHC)-catalyzed synthesis of endo and exo monoacyl-isosorbides (MAIs).

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Valorisation of sludge biomass from civil wastewater

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The growing consumption of energy worldwide, the depletion of fossil fuel resources and global warming have long been encouraging the use of renewable sources such as biomass to meet energy demand. With a circular economy vision, the valorisation of secondary biomass and waste can be a sustainable way to obtain more useful products such as fuels and chemicals. Among the most interesting biomasses are those obtained from sludge produced in civil and industrial wastewater treatment plants. With the growing increase in the number of waste water treatment plants and increasingly stringent rules for the discharge of effluents, the sludge production rate is expected to increase. Traditional technologies are currently focused on the degradation and minimization of the sludge volume. However, the sludge biomass contains a significant concentration of organic carbon which during the pre-treatment could be valorised into bioproducts.

This work presents an approach to the valorisation of sludge from civil wastewaters and the results of hydrothermal pre-treatment tests on them. The purpose of the pre-treatments carried out was to maximize the solubilization of organic carbon in the aqueous phase as well as reduce the volume of sludge. In the liquid fraction the concentrations of total and volatile solids, total organic carbon, chemical oxygen demand (COD), nitrogen, total phosphorus and carbohydrates were studied.

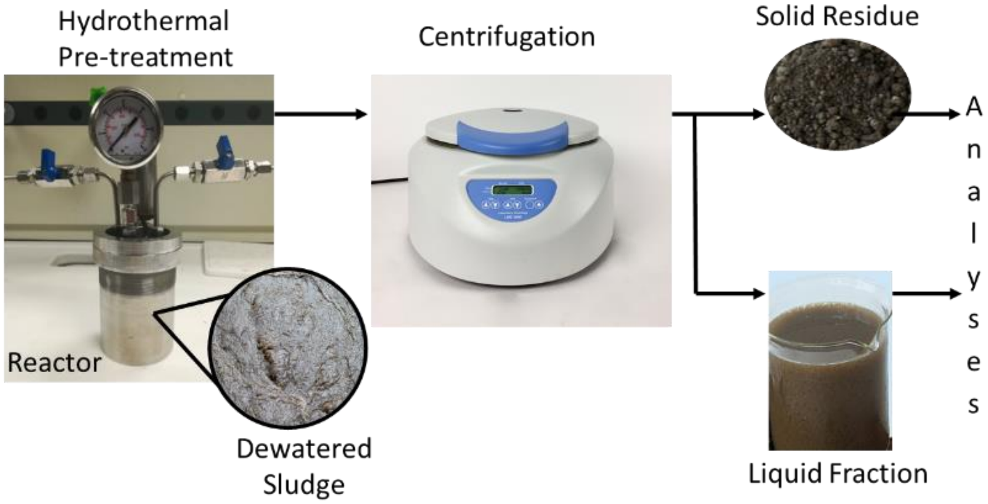

Figure 1. Scheme for hydrothermal pre-treatment of dewatered sludge

Polyhydroxybutyrate as a sustainable platform for the production of chemicals and bio-polymers

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Polyhydroxyalkanoates (PHAs) are biobased and biodegradable polyesters of hydroxy acid monomers bio-synthesized by different kinds of bacteria through the aerobic conversion of various feedstock, and potentially capable to replace fossil-based plastics thanks to similar mechanical and physical proprieties. The development of technologies that allow the production of this biopolymer from wastes through the use of mixed microbial cultures, can open the possibility to produce PHA in a more economically sustainable way. In the context of PHA recycling and valorization, our research group is developing new strategies for: i) recycling the homopolymers polyhydroxybutyrate (PHB) into newly PHB; ii) using PHB as a sustainable platform for the synthesis of chemicals that can be used in the same PHB production cycle (e.g. highly efficient solvents for PHB recovery: MHB and MMB) or iii) for totally different applications, such as the synthesis of high value molecules[1] or the manufacturing of new polymers.

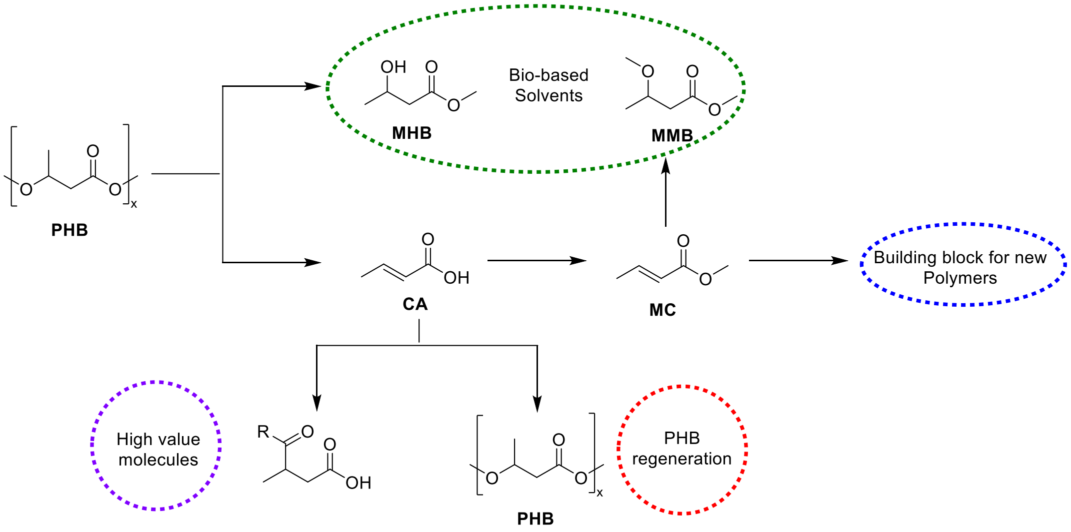

Figure 1. Synthetic routes for PHB recycle and valorization

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Green amination strategies for the production of biobased building-blocks

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Biomass-waste valorisation and the use of sustainable processes are pillars of green chemistry. Cellulose and sugars are the most common biomasses available. Several lactones can be obtained from them, in particular γ-valerolactone, γ-butyrolactone and others. These molecules can be upgraded towards new biobased monomers such as alcohols and amines that are ubiquitous in today's chemical industry, in particular in polymer production. Therefore, it is of paramount importance to find alternative greener synthetic pathways to produce them. Heterogeneous supported copper catalysts could be the tool for the production of these chemicals. The use of copper on various supports will avoid toxic and expensive noble metal catalysts.

The first part of this work concerns studies on hydrogenation reactions of γ-valerolactone (GVL) in order to obtain 1,4-pentanediol (1,4-PDO) with high yield and selectivity. Copper catalysts prepared by the Chemisorption Hydrolysis (CH) method[1] on moderately acidic support such as silica can effectively and selectively promote the hydrogenation of GVL to 1,4-PDO in the green solvent CPME ($P(H_2) = 50$ bar, $T = 160°$ C). This hydrogenation reaction could be strongly driven by the choice of the silica support with different wettability and acidity properties. Two catalysts, namely CuO/SiO_2 A and CuO/SiO_2 B, supported on a less (SiO_2 A) and on a more hydrophilic (SiO_2 B) silicas, were tested in the hydrogenation reaction achieving the 78% yield with the catalyst supported on less hydrophilic silica (CuO/SiO_2 A). It seems that, likely, an unfavourable interaction of the 1,4-PDO product with the catalyst surface may lower the chance of secondary reactions. Moreover, a lower number of strong acid sites in the reaction solvent of CuO/SiO_2 A respect to CuO/SiO_2 B could inhibit side reaction such as dehydratation to Me-THF and the formation of esters. Furthermore, a higher copper dispersion determined by XPS on CuO/SiO_2 A at the surface of the catalyst could explain the high hydrogenation activity.

The work will continue on the further upgrading mono and bialcohols transforming them into amines. The main two synthetic strategy will be hydrogen-borrowing amination pathways due to the non-use or reduced use of hydrogen with the related benefits for both costs and hazard issues. Amination of alcohols with ammonia can be achieved with this strategy using copper catalyst supported on Al_2O_3 prepared with CH method. In the first place, different monoalcohols were tested initially to understand reaction mechanism such as 1-octanol, 2-octanol, cyclooctanol namely a primary, a secondary and a cyclic alcohol. A conversion up to 98% was achieved in the case of secondary and cyclic alcohols obtaining primary and secondary amine as main products. The final aim is to apply this synthetic strategy also to bialcohols such as 1,4-pentanediol and 1,4-butanediol.

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Comparison of rapid calibration models to predict the composition of biomass based on FT-NIR, FT-IR and solid-state NMR

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Approach and aim:

The lignin-to-liquid method (LtL) is a hydrothermal liquefaction method developed at the Department of Chemistry UiB, using water as a reaction medium and formic acid as a catalyst to yield a gas phase, aqueous phase, oil phase and a solid phase. The yield and chemical composition of the bio-oil produced by hydrothermal liquefaction is complex, varying and are highly dependent on reaction time, temperature, and feedstock. To optimize this process, these variables need to be studied further. This article will aim to compare different rapid analyzing techniques in their ability to predict lignocellulosic biomass composition based on 36 different samples of biomass. Using the prediction methods that proves viable, a correlation between biomass composition and bio-oil composition will be the next step. Models to predict composition and yield of bio-oil based on the feedstock have the potential to provide large scale biorefineries an opportunity to adjust the process conditions in favor of the desired end products.

To cover a large variability in the correlation model, samples from three different trees; spruce, birch and pine growing naturally on the coast of Western Norway are further fractionated into heartwood, bark, twigs, and leaves/needles, yielding a total of 36 different samples. The samples set can thus also be a source for further elucidation of the variability of chemical composition within and between different species or different parts of trees.

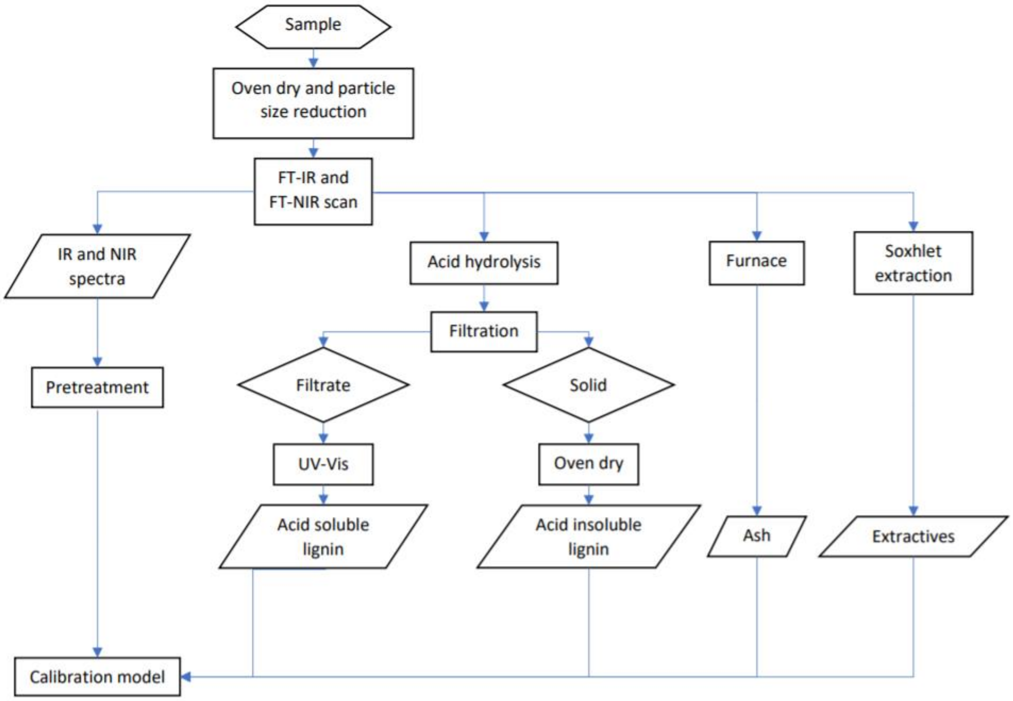

Figure 1: Flowchart of the preparation procedure.

Scientific innovation and relevance:

The initial aim is to create a correlation model based on spectroscopic data. This is done by recording NIR, IR and NMR spectra of the samples. Spectra of both coarsely ground and finely ground samples are performed to further enhance the predictive power. For a large-scale on-line process monitoring setting, it would be beneficial if coarsely ground biomass is sufficient to predict of the overall chemical composition. Next, chemical degradation of each sample is performed to determine the ratio of carbohydrates, lignin, ash, and extractives. The spectra are then used as dependent variables to predict the different ratios of constituents in the biomass. No previous studies have compared data from different spectroscopic techniques to evaluate how to get the most reliable prediction models.

Preliminary results and discussion:

Though different spectroscopic procedures have been used for biomass characterization, they have not previously been compared. In this work, the predictive power of the different methods and their combinations will be evaluated and considered with respect to a large-scale scenario, investigating cost, effectiveness, and viability for thermochemical biomass conversion.

Chemical degradation of the samples shows that the biggest variation in the chemical composition lies between fractions more than tree species. Principal Component Analysis (PCA) for the IR and NIR spectra made the fractions highly distinguishable, and no particular groupings for tree species. Partial Least Squares (PLS) calibration models for prediction of lignin based on IR and NIR spectra give reasonable results. The root mean square error of cross validation (RMSECV) of the calibration using IR and NIR spectra are 7,60 w/w% and 6,42 w/w% respectively, giving NIR a slight edge.

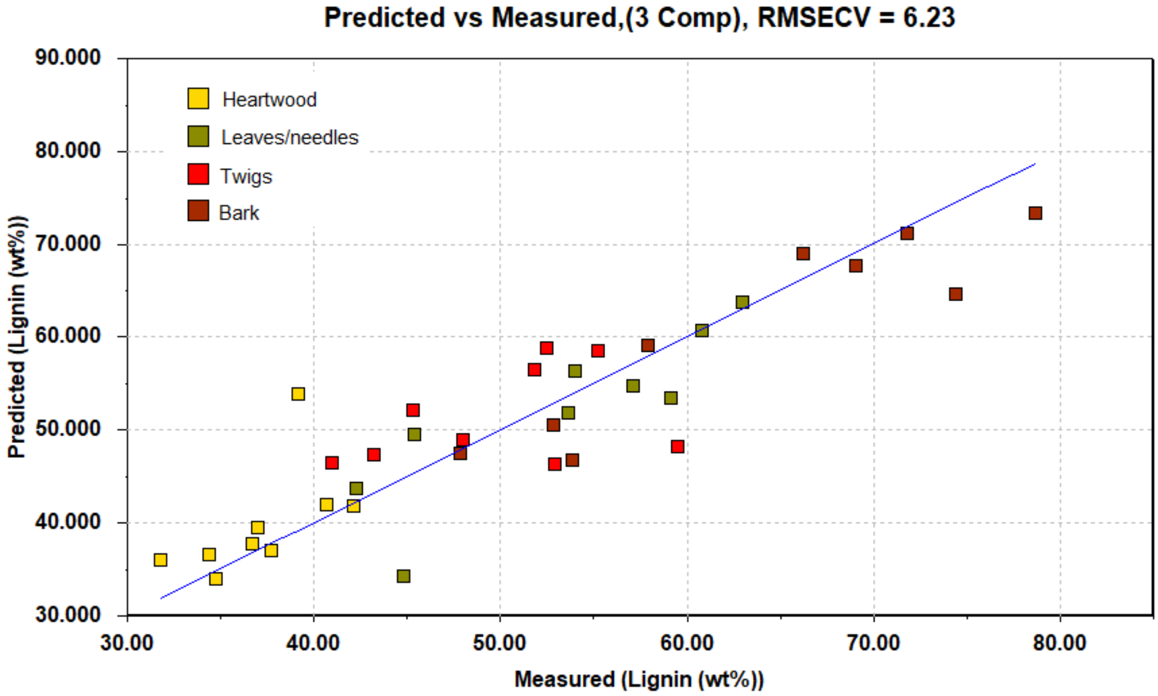

Figure 2: Predicted value plotted against measured value of lignin content for NIR spectra based on PLS regression.

Carboxymethyl chitosan films – properties

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Chitosan is a biodegradable biopolymer. It is obtained from post-production waste such as crab or shrimp shells. It is insoluble in water. Carboxymethyl chitosan is a biocompatible, biodegradable derivative of chitosan. It is also non-toxic and water-soluble and has antibacterial properties.

The aim of the study was to compare properties of chitosan and carboxymethylchitosan thin films. Thin films were prepared on PS plates. Analyzes as scanning electron microscope analysis, atomic force microscope analysisand a Zwick & Roell Z.0.5 testing machine was performed. Changes in morphological and mechanical properties were observed.

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Ecological dyeing of natural fabrics with renewable raw materials-plant derived colorants

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Currently the most of society is aware of how important is sustainable development, the ecological approach in many different industries and using renewable and green raw materials, which is of interest to green chemistry. The application of natural and renewable materials or ingredients and the need to create various products not contributing to the destruction of the environment are renewed today.The majority of industries are becoming more ecological, less harmful for the environment and healthier for consumers. In various areas for example in cosmetics, food, textiles, leather or paper industries several colorants are widely applied. It is estimated that the textile industry consumes one of the greatest amounts of colorants, but mainly synthetic ones are used to impart the desired color to different fabrics. However, they can have unfavorable environmental and health effects. Also, their receipt is associated with numerous stages and reactions contributing to the consumption of toxic or not environmentally friendly substances and solvents. Plant derived colorants as a renewable and green source of color may provide a healthier alternative not only for society but also for the environment. They are biodegradable, known for thousands of years, do not pollute the environment and do not require the usage of harmful solvents and substances. Besides dyeing ability, botanical colorants have various other properties like antimicrobial or antioxidant, which are their additional benefit of the application. Those colorants are successfully applied in food but have also potential to be successfully applied in the textile or even cosmetic industry, both products present in the life of almost every person. Various types of fabrics can be dyed with plant derived colorants or even agro industrial byproducts, but their instability under conditions like pH, temperature, UV radiation and storage limits their widespread use.

The study focuses on the application of botanical food colorants in one of the most dye-consuming products like fabrics as an green alternative to synthetic colorants leading to more sustainable development. In the study different types of fabrics for instance cotton, linen, silk and leather were dyed with plant derived food colorants consisting mainly of fruits and vegetable extracts without inorganic mordants. Various colorants concentrations, dyeing conditions and additionally a 1% chitosan solution and a 20% shellac solution were applied. The effect of colorants and additives were studied on fabrics dyeing, colorfastness and their mechanical properties like tensile properties. To examine colorfastness under the influence of light the colored samples of fabrics were treated with UV radiation. The effect of washing on dyed fabrics was also tested. Colorimeter and ATR-FTIR measurements were performed. It was found that not all plant derived food colorants were appropriate for fabrics dyeing. A 1% concentration of colorants was sufficient to dye fabrics, but in the case of leather higher concentration was required (5%). However, after washing, the color fastness of dyed fabrics deteriorated significantly, also with chitosan addition. After 4 hours of UV irradiation, all fabrics showed the change in color shade, but the dyed cotton showed the poorest colorfastness. Chitosan treatment and shellac covering influence the tensile properties of materials.

Outline of a Process for the Hydrothermal Liquefaction of a Tannery Sludge for Biofuel Production

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Hydrothermal liquefaction (HTL) is a promising technology to simultaneously reduce the amount of waste disposed of in landfills and produce biofuels from renewable sources or, more in general, liquidphase energy carriers from non-traditional organic feedstocks [1]. During the HTL process, water in the liquid phase at temperature and pressure of about 200–350 °C and 40–200 bar, respectively, promotes (acting as solvent, reaction medium and thermal flywheel at the same time) the conversion of the biomass feedstock into bio-crude (also termed bio-oil) as the target product [2]. Aqueous phase, biogas and biochar as co-products are also produced. Bio-oil formation is favoured by sub-critical water properties in the temperature and pressure ranges of interest for HTL. In fact, under these conditions, the water ionic product is high enough to promote ionic reactions leading to the formation of the bio-crude. Moreover, the values of the dielectric constant determine for water the polarity characteristic of organic solvents, thus promoting the decomposition via hydrolysis of the organic fragments of the starting biomass, which in turn undergo dehydration, decarboxylation and deamination reactions [3]. Finally, fragments can repolymerise to give the biocrude. Several types of biomasses are studied in literature as feedstock for HTL processes, such as algae, lignocellulosic residues, waste, sludge, etc. Sewage sludge is an attractive material for HTL due to its physico/chemical characteristics and high-water content [4]. In fact, in traditional thermo-chemical processes for energy conversion such as gasification, pyrolysis, torrefaction etc., the high moisture content of the sludge makes this material unattractive due to the requirement of an energy intensive vaporisation step [5]. On the contrary, for the HTL process, this factor turns out to be an added value because liquid water is needed to perform the HTL process. In this context, industrial sludges are of interest for HTL, which offers the chance of both reducing sludge disposal and obtaining bio-crude [6]. The aim of this work is to characterise an industrial tannery sludge to determine its composition, energy properties and microstructure prior to its energetic valorisation by means of the HTL process. In particular, proximate and ultimate compositions, higher heating value, metal content by ICPMS and crystalline phases via XRD analysis have been determined. Results show that the starting sludge is characterised by a 34$\%_{\mathrm{wt.}}$ carbon content, and its higher heating value is about 15 MJ/kg on a dry basis. These values confirm the possibility of considering the tannery sludge as a promising energy carrier in valorisation processes. A lab-scale plant was purposely designed (Figure 1) to perform HTL kinetic tests under different operating conditions (temperature, pressure, heating rate and biomass-to-water mass ratio), so to also elucidate the reaction mechanism and identify optimal operating conditions for obtaining a high-yield bio-crude with more attractive energy properties. In particular, the HTL reactor is a 500 mL batch autoclave, made of nickel-chromium molybdenum alloy (Hastelloy C–276). This alloy was chosen as it is particularly resistant to harsh process conditions allowing to avoid corrosion phenomena that could occur on the reactor walls under subcritical HTL conditions. Finally, to investigate the relationships between HTL operating conditions and yield/quality of the sludge-derived bio-fuels, an original elaboration of literature data was performed.

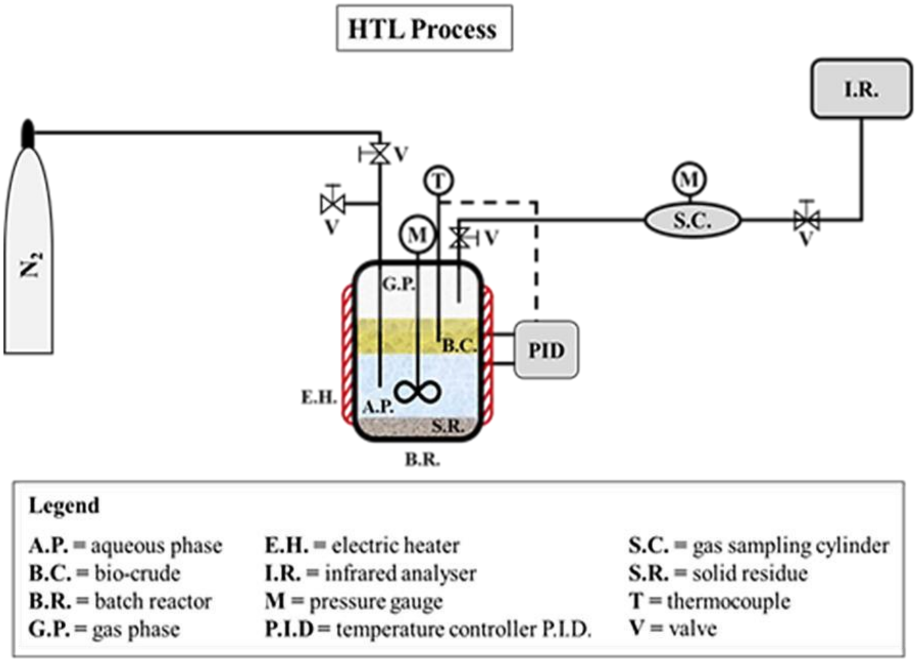

Figure 1. Layout of the lab-scale apparatus for the execution of HTL tests.

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Recycling Agricultural Wastes and By-products in Organic Farming

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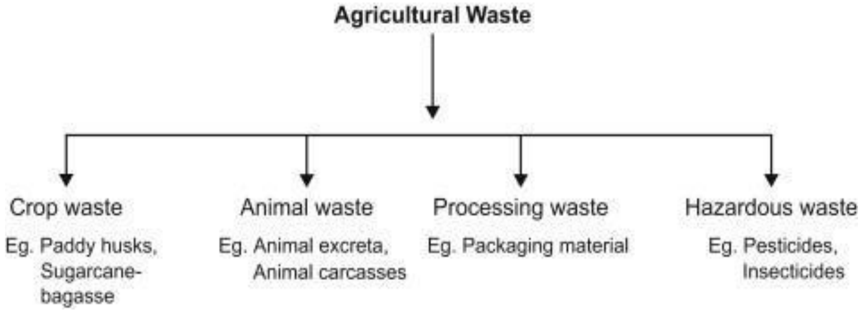
The Circular Economy concept implies the re-design of existing production systems in agriculture, by promoting agricultural waste recycling. two different agroecological tools were considered: biofertilizer and presence or absence of green manure (GM+ and GM−). Moreover, the microorganism activity lasts for the whole composting process, where microorganism digest or decompose organic matters. therefore, as one of economical agricultural waste disposal method, composting is only suitable for organic agricultural solid waste.

And the organic agricultural waste can be: (i) Organic waste from farmland: Straw, wheat straw, corn straw, vegetable leaves; (ii) Animal farm organic waste: Chicken manure pig manure, cattle manure, horse manure, sheep manure; (iii) Organic waste from plantation: Leaves and small branches, rotten fruit. Therefore, the common agricultural waste disposal methods include burning, dumping, land filling, random piling. All these methods may cause pollution and waste of resources. Above mentioned wastes contain multiple nutrient elements, which can be made into organic fertilizer. meanwhile, the organic fertilizer can be used for agricultural production again. Therefore, it is an economical and environmentally friendly agricultural waste disposal method to deal with waste by composting.

Keywords: microorganism digest; biofertilizer; economical agricultural waste; Organic waste.



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Bio-based and eco-friendly products as efficient alternatives to commercial biocides for the production of sustainable sol-gel based antifouling coatings

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Since ancient times, the adhesion of marine fouling organisms on surfaces, such as ship hulls, has represented an important issue, mainly because of the extra energy consumption, high maintenance costs, and increased corrosion. Nowadays, this problem has been mitigated by treating vessel surfaces with different types of antifouling paints. However, all of these coatings have one thing in common, that is the tendency to release toxic metals in the marine environment. Despite the fact that in 2008 tributyltin-based products have been banned by the International Maritime Organization (IMO), biocide-release paintings based on metals have been still used in today's marine applications. In particular, cuprous oxide antifouling coatings are among the most employed, posing serious potential environmental risks. With the aim of preventing the antifouling paints from destroying the ecological environment and harming human health, worldwide researchers have tried to find functional substances from nature, thus replacing copper-based finishing. In the last years, natural products have been recognized as important sources of antifoulants, presenting some important advantages, such as low cost, no toxicity and ready availability in nature.

In this work, an eco- friendly solution to the marine fouling issue has been proposed. The as-prepared coating consists in a sol-gel based formulation, including both a non-toxic biocide, present in the BPR list, and a natural product. The adopted synergistic antifouling strategy, aimed to discourage the growth of marine organisms on the surface, exploited both the effect of the silicone-based coating, that is the low energy surface and the biocide-release action of the active ingredients. The sol-gel based formulation, before being applied on the material surface, has been thorough studied and its chemical structure as well as its properties have been investigated by means of different chemical-physical techniques. Also preliminary biological tests have been carried out in order to assess the resistance of the as-prepared coating against various types of microorganisms, such as fungi and bacteria. Antifouling tests have shown that the sol-gel coating can be efficient in decreasing the biofouling phenomenon.

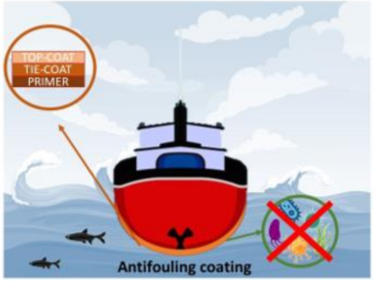

Figure 1. Treatment of ship hull with antifouling painting

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Adding value to pulp industry waste: Bio-based thermosetting epoxy resins using Kraft lignin

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Lignin is one of the three main structural components of lignocellulosic biomass, representing the most abundant natural source of aromatics and phenolics. Technical lignins like Kraft and lignosulfonate lignin are recovered in huge amounts (Mtons/year) as side products in the pulp and paper industry. However, they are highly underutilized in the currently available biorefinery schemes as they are traditionally used for the in-house production of heat and energy [1]. Its high aromaticity and hydroxylated surface offer the possibility to be utilized in the production of new bio-based polymers, such as epoxy resins or be used as a green bio-based additive in polymer blends and composites. Epoxy and phenol-formaldehyde resins have been studied as potential substrates for addition of lignins [2]. Lignin due to its highly versatile structure can be used without any modification or after various treatments, e.g., mechanical or chemical modifications (glycidylation, phenolation, amination etc.) or after fractionation using appropriate solvents.

In this work, Kraft lignin was utilized for the production of lignin-based epoxy composites. Kraft lignin was used either as received or after chemical or mechanical treatment/fractionation that included solvent fractionation, glycidylation and ball milling. Micro-sized lignin was obtained after fractionation of kraft lignin in ethanol while lignin's functionalization with epoxy rings (glycidylation) was achieved via reaction with epichlorohydrin in a methanolic sodium hydroxide (NaOH) solution at 80^{o}C. Ball milling to further reduce the size was performed for 2 and 8 h. Structural and morphological characteristics of initial and treated lignins were investigated using GPC, NMR, SEM, PSD etc. Epoxy blends were prepared using commercially available epoxy resin, i.e., diglycidyl ether of bisphenol A (DGEBA) and Jeffamines D-230 (glassy system) and D-2000 (rubbery system) as curing agents. The composites were prepared by in-situ polymerization, followed by curing at selected conditions. The mechanical properties of the prepared composites were tested using tensile test measurements.

The utilization of Kraft lignin as curing agent was successful in both glassy and rubbery epoxy composite systems. In the rubbery lignin/epoxy composites containing initial and treated kraft lignins, a substantial increase in the mechanical properties was achieved at low lignin loadings (3 wt.%), while increase of lignin loading resulted in further improvement in strength, elongation and stiffness. Interestingly, up to a 34% replacement was achieved with the rubbery epoxy composites leading to improved stress, stiffness and strain before break. The glassy epoxy composites containing initial kraft lignin and all treated lignins (micro-, ball milled- and glycidylized lignins) as fillers exhibited increased strength and stiffness at low loadings (3 wt.%).

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Plant metabolites as stimulants and/or inhibitors of parasitic plant seed germination

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Broomrapes (*Orobanche* and *Phelipanche* spp.), are holoparasitic weeds that severely infesting a large number of important crops and causing severe yield losses. The main obstacle for long-term management of broomrape infested fields is the durable seedbank with evolved mechanisms of host recognition upon perception of host-derived germination factors. The continuous spread of broomrapes strongly affects the farmers work as heavy infestations lead to a complete crop loss and have a great negative impact over many years. In fact, parasitic seeds can survive in soil for decades until the germination is induced by a chemical signal exuded by the root of the host plant. Current control methods relies on the use of resistant crop varieties and herbicides, albeit success has been marginal. Considering that seed germination is a key phase for parasitic plant development and infestation, a further approach proposed for the management of these weeds has been to use microbial or plant metabolites to stimulate in absence of the host (the so called "suicidal germination) and/or inhibit the broomrape seed germination. Some metabolites induced a rapid cessation of radicle growth with the promotion of a layer of papillae at the radicle tip hampering the contact of the parasite to the host. The development of herbicides based on natural metabolites from wild plant, targeting early stages on parasitic plant development, might contribute to the reduction of broomrape seed bank in soils. This research is innovative as it proposes an alternative method to the massive use of synthetic herbicides for the management of parasitic plants. Natural inspired herbicides could reduce the environmental impact and consequently the risks for humans and animal health.

This communication will illustrate the preliminary results on the isolation and chemical characterization of metabolites extracted from root of seventeen weed plants and the results of testing them on the seed germination of different broomrape species.

2. NEW REACTION PATHWAYS

Efficient degradation of Carbamazepine (CBZ) from waste water using combined effect of immobilized laccase and ultrasound

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Carbamazepine (CBZ), an intractable pharmaceutically active compound that has a critical impact on aquatic life and health risks caused to humans, is widely detected in wastewater due to its persistent nature towards conventional wastewater treatment methods. This made it imperative to the design of a standard protocol and new treatment scheme. An efficient laccase immobilized magnetic nano-biocatalyst for the degradation of carbamazepine (CBZ), was constructed by the immobilization of laccase on magnetic nanoparticles using glutaraldehyde as a cross-linker. The characterization of the prepared biocatalyst was carried out using FTIR, XRD, SEM, CLSM and VSM analysis. Spherical biocatalyst with an average diameter <100 nm was synthesized showing supermagnetic behavior with saturation magnetization of 35.85 emu/g. Immobilized laccase showed optimum pH 5 which was similar to free laccase however, the optimum temperature of free laccase was 50 °C which shifted to 60 °C after immobilization. The synergistic effect of ultrasound and immobilized laccase for the degradation of CBZ was studied. The optimization results showed that maximum degradation of CBZ (>95%) was observed at 20 W ultrasound power, 3% (w/v) enzyme loading and 20 min treatment time. Immobilized laccase showed improved thermal kinetics with higher temperature and pH resistance, making it a more robust biocatalyst. Immobilized enzymes were recycled upto 10 cycles and can be stored for 45 days, maintaining the residual activity of more than 90%.

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Understanding the mechanism of Ir(III) catalyzed CO_2 hydrogenation in water

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CO_2 which is one of the greenhouse gases obtained from anthropogenic sources serves as one of the causes of global warming. By hydrogenating CO_2 to various products such as formates, methanol and dimethyl ether, CO_2 can be valorized while at the same serving as a means of H_2.[1-3] Several iridium(III) complexes that posses, rigid, bulky, electron-rich, proton-responsive OH or NH groups N^N bidentate ligands have served as effective catalysts for carrying out various CO_2 transformations due to in situ deprotonation of the ligands.[4,5] Here-in we report the synthesis of a series of N^N bidentate tetrazolyl ligands and their corresponding iridium(III) complexes with and without proton responsive OH and NH groups (**Figure 1**). In the absence of proton responsive groups, different mechanisms of hydrogenation are observed as opposed to the presence of proton responsive groups. *In situ* ^{1}HNMR experiments demonstrate the formation of catalytically active iridium-hydride specie through initial generation of a bridged Ir···H···Ir intermediate. Subsequently, the reaction proceeds by direct CO_2 hydrogenation or pre-formed $NaHCO_3$ reduction with likely intermediates being observed experimentally.

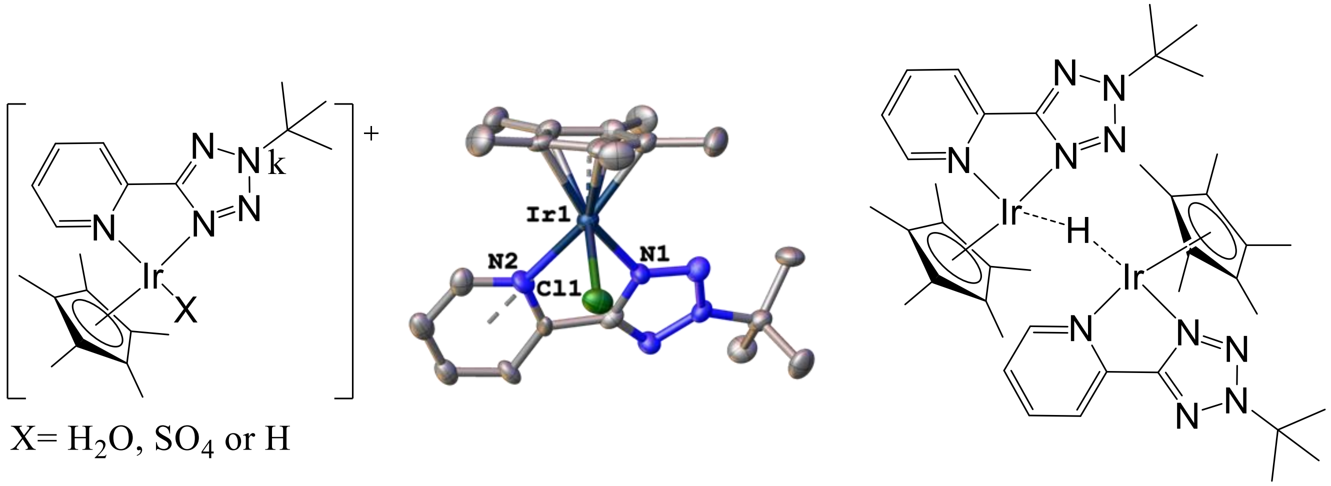

Figure 1: CO_2 Hydrogenation using Iridium tetrazolyl complexes

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Synthesis, crystal structures and photocatalytic study of coordination polymers constructed from tetracarboxylate ligand

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Photocatalytic degradation of pollutants present simple, economical and efficient ways of remediation of harmful pollutants found in industrial wastewater [1]. Coordination polymers are preferred to conventional photocatalysts like TiO_2 as they possess lower band gaps, making them suitable for use under solar radiation [2]. Coordination polymers $[Mn_2(btec)]_n$ (**1**), $[Ce_2(H_2btec)(btec)(H_2O)_2]_n$ (**2**) and $[Fe(Hbtec)_2(H_2O)_2]_n$ (**3**) (btec = 1,2,4,5-benzenetetracarboxylic acid) [3] were synthesized hydrothermally, using distilled water only as the solvent. They were characterized using CHN analysis, spectroscopic and X-ray diffraction techniques. **1** was also characterized by single crystal X-ray crystallography. Mn(II) and Fe(III) centres in **1** and **3** exhibit octahedral geometry, while both Ce(III) centres in **2** are nine-coordinate, exhibiting tricapped trigonal prismatic geometry. Tauc plots from Diffuse Reflectance UV-Vis spectral data reveal band gaps in the range 2.87- 3.61 eV for the compounds. Photocatalytic degradation efficiency of methylene blue solution under solar radiation (with environmentally benign H_2O_2 as electron acceptor) was 85%, 95% and 100% for **1, 2** and **3** respectively in 150 minutes, with **3** achieving 50% degradation in 30 minutes. Active specie trapping experiments showed that the holes, hydroxyl and superoxide radicals were responsible for the degradation. The outstanding results obtained show that the compound could be useful in the development of efficient solar-photocatalysts.

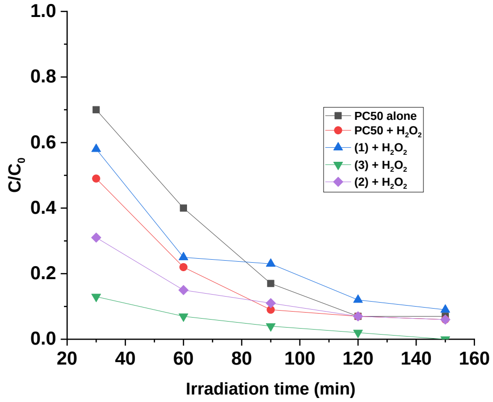

Figure 1. Comparison of the degradation efficiency of the photocatalysts and PC50 (commercial TiO_2).

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Metal-free, highly soluble, fully aromatic fluorinated ladder polymer

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New high molecular weight, aromatic fluorinated ladder polymer has been obtained by superacid catalyzed non stoichiometric step-polymerization of xanthenediol with trifluoroacetone. The polymerizations carried at different concentration de monomer out at room temperature in a mixture of trifluoromethanesulfonic acid (CF_3SO_3H, TFSA) with methylene chloride resulted in a polymer completely soluble in acetone, methylene chloride, chloroform, THF, methanol, DMFA, NMP, DMAC, in all cases. The chemical composition of the ladder polymer has been confirmed by the complementary experimental and calculations studies of the^{13}C and ^{19}F NMR spectra and the calculations of reaction pathways. Flexible, elastic films were obtained by casting. According to gas permeation experiments, the ladder polymer falls above the Robeson´s 2008 updated upper bound. When treating the polymer in different solvents (e.g. THF, acetone or methanol) its porosity is affected, based on surface area experiments (BET area).

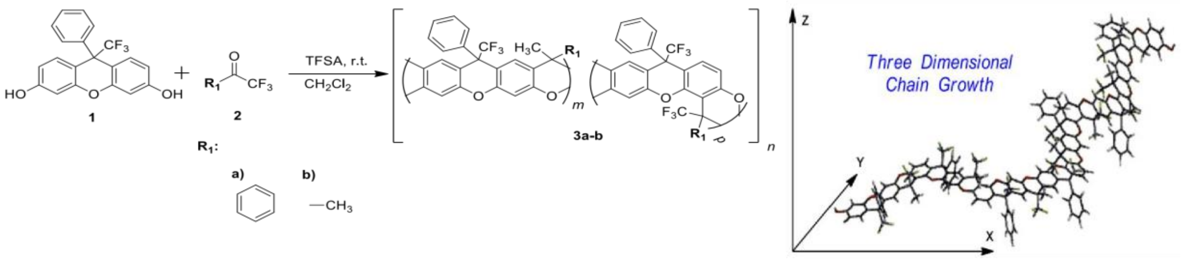

Figure 1: General reaction.

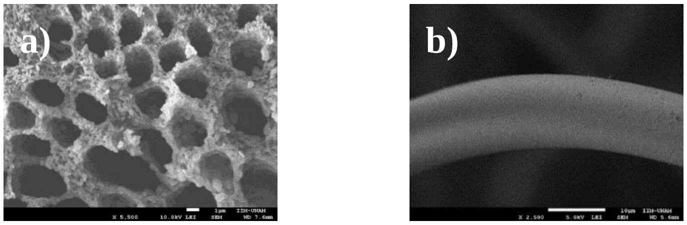

Figure 2: a) Ladder polymer **3a** in acetone; b) Ladder polymer **3a** in THF.

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Efficient solvent-free hydrogenation of bio-derived furfural to furfuryl alcohol by Copper Metal Organic Framework

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Metal Organic Framework (MOFs) are heterogeneous, porous crystalline materials composed of metal ions or clusters and organic ligands which are connected through metal-ligand coordination to form three-dimensional (3D) coordination networks.[1,2] These materials have a high surface area, good stability, highly ordered structure, a compositional diversity, which can be precisely tailored and are inexpensive.[3-5] MOFs have the advantage that their pore/chemical environment can be changed either by functionalizing the organic linker or metal nodes resulting in good catalytic activity. In this work, copper MOF has been synthesized and characterized X-ray diffraction studies (powder X-ray diffraction, single crystal X-ray diffraction), and thermal analysis (thermogravimetric analysis, differential scanning calorimetry). The MOF was evaluated as catalyst pre-cursors using formic acid as a hydrogen source. The catalytic system resulted in good activity and exclusive selectivity towards furfuryl alcohol in the hydrogenation reaction.

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Visible light to generate excited anion radicals of Naphthalene Diimides

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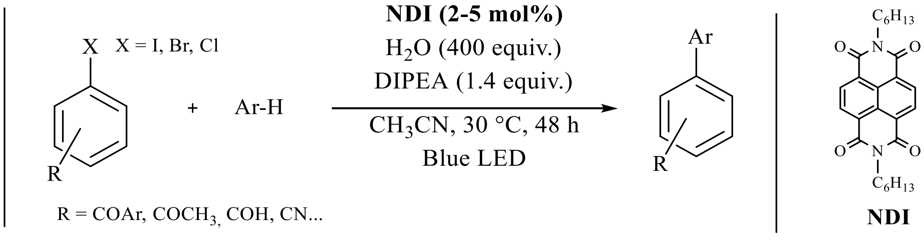
In the present work I introduce the currently study of a photostimulated reaction using a synthesized photocatalyst under visible light irradiation. As it is well known, photostimulated reactions are a representative example into the development of environmentally friendly methodologies: light is a clean reactive without residual waste.

The versatility of this approximation applied to the synthesis of valuable organic compounds has been demonstrated in several occasions. An interesting proposal was done by König et al. who generated aryl radicals from aryl halides through two consecutive photoinduced electron transfer (conPET) using perylenediimide (PDI) as catalyst.[1]

With these achievements on mind, we synthesized a family of naphtalente diimides (NDIs) to be used in a conPET approach. Our recently accepted results[2] demonstrated the ability of these catalysts for achieve a C-C bond formation under visible light through the formation of their excited radical anions (NDI•–*) with moderated yields. This demanding photocatalytic transformation was parallel studied under a photo-electrochemical approach having comparable yields with more selectivity. Regarding to the reaction mechanism, further studies have done including spectroscopic measurements which confirm a conPET process.

Having these results, we started new explorations of the reactions conditions with the aim of achieve complete conversion of the substrate in a model system (Scheme 1) and extend its synthetic utility. Our first results into the ongoing work show better conversions when water is added to the photocatalytic system and less charge of photocatalyst is used (compared to previous experiments). With the best condition in hand, we started to explore the scope of the reaction of homolytic aromatic substitution trying substrates with several substituents.



Scheme 1. Reaction conditions in study.

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Biocatalytic approach for enantiomeric resolution of benzothiazolines and benzoimidazolines using MAO enzyme

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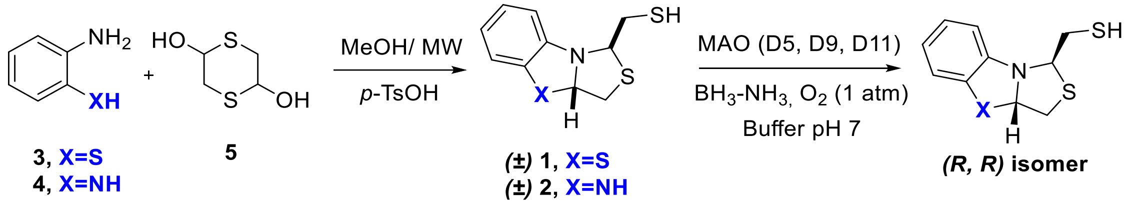
Benzothiazolines **1** and benzoimidazolines **2** are tricyclic compounds designed as penicillin analogs, which demonstrated competitive inhibition of all Metallo-beta-lactamases (MBL) subclasses, with *Ki* values in the micromolar range. These compounds are obtained in a single step starting from 2-aminothiophenol **3** or 2-aminoanilines **4**, respectively, and dithiane **5**, see Scheme 1.



Scheme 1. Synthesis and enantiomeric resolution of **1** and **2** using MAO-N.

Despite **1** and **2** resulted to be very good inhibitors against all subclasses of MBL, they are obtained as a racemic mixture. Crystallographic studies demonstrated that (*R, R*) isomer binds preferably with NDM-1 and VIM-2 enzymes, both MBL of clinical importance. For that reason, we aimed to develop a strategy for enantiomeric resolution of **1** and **2**.

Since the mercaptomethyl group present in **1** and **2** is essential for MBL inhibition, it must be preserved during the deracemization process. Compared to non-enzymatic chemical catalysts, biocatalysts are known to present some interesting and advantageous features: high efficiency, mild environmentally-friendly operation conditions, versatility and high selectivity.[1]

Turner's group reported a method for deracemization of primary, secondary and tertiary amines using variants of monoamine oxidase (MAO) from *Aspergillus niger* which display remarkable substrate scope and tolerance for sterically demanding motif.[2,3] We envisioned that this methodology could be useful and applied for enantiomeric resolution of our products. Thus, the racemic mixture was subjected to a deracemization protocol using *E. coli* whole cells expressing three different MAO-N variants and MAO-N purified enzymes. No resolution was found for **1** when using all three variants. On the other hand, all three D5, D9 and D11 variants resulted to be enantioselective for **2**. D11 variant showed the best result, providing the optically enriched product in excellent enantiomeric excess (90%) after 4 hours of reaction. Currently, we are optimizing the parameters to scale up the reaction.

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Green synthesis of ZnO coated hybrid biochar for the synchronous removal of Ciprofloxacin and Tetracycline in Wastewater

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Biochar prepared from Kaolinite and coconut husk (KCB) and further activated with HCl (KCB-A) and KOH (KCB-B) via microwave technique for the remediation of Ciprofloxacin (CIP) and Tetracycline (TET) from water were carried out. Characterization using scanning electron microscopy, energy dispersive X-ray, Fourier transform infrared spectroscopy and X-Ray diffraction showed the successful synthesis of functionalized biochars. Batch adsorption experiments demonstrated the potential of the adsorbents for fast and efficient removal of CIP and TET from solution. Adsorption capacities were found to be 71, 140 and 229 mg/g for CIP and 118, 117 and 232 mg/g for TET removal on KCB, KCB-A and KCB-B respectively. For KCB, KCB-B and KCB-B, CIP adsorption best followed the pseudo second order (PSOM), pseudo first order kinetic model (PFOM) and Intraparticle diffusion (IDP) respectively. TET adsorption followed PSOM for KCB, IPD for KCB-B and PFOM for KCB-A. CIP adsorption on KCB, KCB-A and KCB-B best fit the Temkin, Langmuir and Brouers-Sotolongo isotherm respectively and TET adsorption on KCB best fit Brouers-Sotolongo while KCB-A and KCB-B best fit Langmuir-Freundlich. Adsorption of both contaminants was thermodynamically feasible showing that these materials are excellent adsorbents for the treatment of pharmaceuticals in water.

Keywords: Ciprofloxacin, Adsorption, Functionalised biochar, Coconut husk, Kaolinite, Tetracycline

Condensation Reactions of Methyl Derivatives of Quinoxaline and Quinoxaline-1,4-dioxide with Aromatic Dialdehyde

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In this research, some condensation reactions have been carried out between 2-methylquinoxaline-1,4-dioxid derivatives and terephthaldehyde and biphenyl dialdehyde. Moreover, 2-methylquinoxaline has been reacted with trerephthaldehyde. The structures of all products have been suggested depending on IR, and NMR spectroscopic methods. Suitable mechanisms have been suggested for their formation. The Quinoxalines derivatives have been prepared from 2-nitroaniline derivatives via Beirut reaction. The products were sparingly soluble in all available solvents. Sulfonation reactions have been tried of products but without reasonable success.

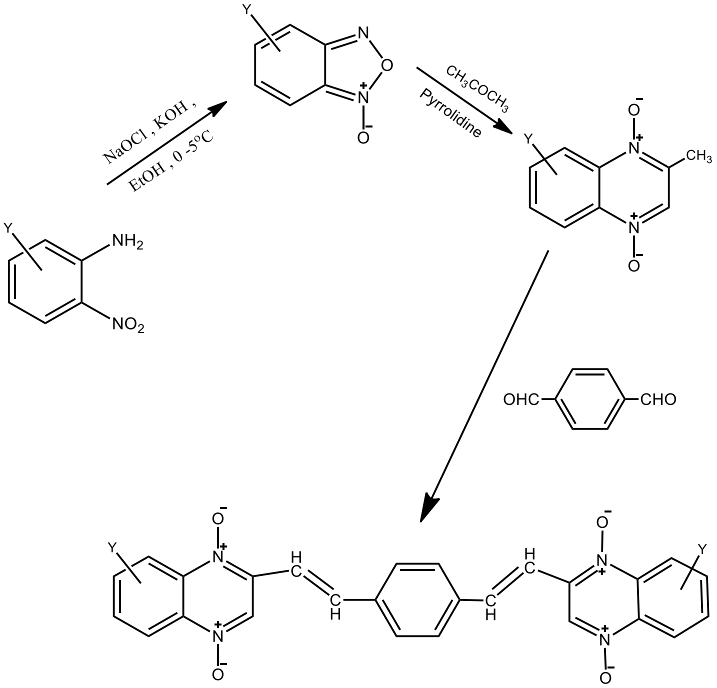

Figure 1. condensation reactions (Started preparing Quinoxaline-1,4 dioxide derivatives from Nitro Aniline derivatives Via Beirut Reaction)

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Facile *in situ* formation of luminescent cellulose paper using a novel solvent-based approach

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Cellulose has become one of the most widely used biopolymers for the development of sustainable technologies. Despite its numerous applications, the poor processability of this polymer, due to a lack of suitable solvents, has hampered the development of more advanced cellulose-based materials [1-2]. This work describes a novel method involving partial dissolution of cellulose by an inorganic solvent, followed by *in-situ* chemical reactions performed on the solvent.

In this study, two functionalised cellulose papers, F1 and F2, were prepared by incorporation of the luminescent copper(I) cluster (Cu_4L_4) *via* two distinct methodologies (L denotes the dithiophosphonate (DTP) ligand of the form $[S_2PR(OR')]^{-}$). The novel approach used to fabricate F1 involves (i) partial dissolution of bacterial cellulose in Schweizer's reagent ($[Cu(NH_3)_4(H_2O)_2](OH)_2$) followed by (ii) simultaneous precipitation and regeneration of Cu_4L_4 and cellulose fibers, respectively, upon addition of an acidic form of the DTP ligand. Physical blending of the pre-isolated copper(I) cluster and the cellulose fibers yields F2.

Scanning electron microscopy (SEM) supplemented with energy dispersive X-ray spectroscopy (EDS), as well as powder X-ray diffraction (XRD), solid-state photoluminescence (PL), and ^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectroscopies were used to investigate the chemical composition and physical morphology of F1 and F2. The results for F1 reveal a uniform distribution of amorphous and spherical cluster particles which are well-embedded within the cellulose matrix. Conversely, significant aggregation and predominantly surface-deposited crystalline cluster particles are observed in F2. Furthermore, solvent stability tests show that F1 is stable in aqueous and alcoholic environments.

Hence, for the first time it has been demonstrated that the solvent system itself can be used as a reagent to introduce homogeneously distributed and robust chemical functionality to cellulose-based materials [3]. Moreover, this novel strategy serves as a facile method by which other inorganic metal complexes (Cu, Cd, Ni Co, *etc.*) with acidic ligand derivatives can potentially be incorporated into a cellulose-based composite, and – in addition to the optical properties exploited here – be applied in the areas of catalysis and possibly biomaterials.

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Keywords: luminescence, cellulose solvents, cellulose composites

Efficiency improvements of CO_2 utilization: the case of styrene carbonate synthesis in microdroplets conditions

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Caterina Rovegno and Daniele Urbani equally contributed to this research.

Microdroplets reactions have recently attracted the attention of the synthetic chemists' community due to the remarkable acceleration [1] caused to valuable transformations by this new methodological paradigm. Various homogeneous liquid phase, and two phases liquid-liquid reactions in inert gas atmosphere have been reported in the literature, representing successful milestones in this field. These results have been justified by specific physical and physico-chemical phenomena originated within or at the microdroplets-gas interface [2]. Furthermore, this novel approach looks particularly promising for biphasic gas-liquid transformations, as recently reported for the water TPPS-mediated $^1O_2$ aerosol photochemical selective oxidation of sulfide to sulfoxide in air [3].
In our continuous efforts to exploit this innovative methodological approach, we herein report our findings in the microdroplets styrene epoxide-to-carbonate conversion in CO_2 atmosphere mediated by potassium iodide/triethylene glycol (KI/TEG) complex (Fig. 1).

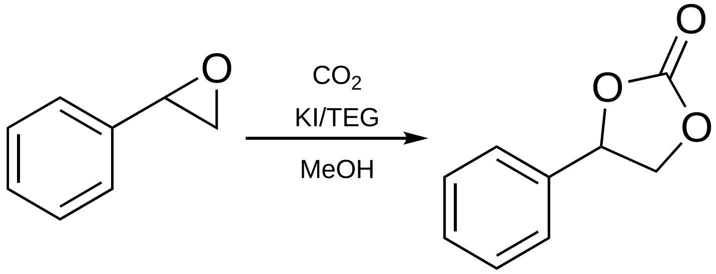

Fig. 1: Scheme of the model reaction

A direct comparison between ordinary bulk *vs* microdroplets reaction at various temperature and conditions will be presented, revealing the beneficial effects of aerosol conditions on reaction rates of the selected model transformation.

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Preparation of single-atom catalysis based on carbon nitride materials

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Lignocellulosic biomass is a promising alternative as a complementary source of oil and might produce biofuels, green solvents and building-blocks for several value-added chemicals. The biomass depolymerization is an important source of sugars, which undergo to several valorization reactions. Among these reactions, the glucose conversion to lactic acid and alkyl lactates is a fundamental route to be studied since very low yields are achieved from glucose fermentation. Lactic acid is a promising building block in the chemical industry e can be converted to a wide range of value-added compounds, such as polylactic acid, acrylic acid and propylene glycol. Alkyl lactates are widely used as green solvents and in the pharmaceutical industry. Despite of the homogeneous and heterogeneous catalysis consist in a step forward to lactic acid production; various drawbacks need to be overcome. The homogeneous catalysis possesses a high difficulty to for the catalyst reuse and thus, creating a large amount of residue. On the other hand, heterogeneous catalysis presents low exposure of the active sites. In this context, single-atom catalysis is very promising since link the advantages of homogeneous and heterogeneous catalysis, such as high exposure of active sites and easy catalyst recovery, respectively. It is important to highlight that, so far, no reports are found in the literature regarding the use of single-atom catalysis for the lactic acid/lactates synthesis from lignocellulosic sugars. Considering the aforementioned explanations, this research project aims the preparation of single-atom catalysis based on carbon nitride materials – an efficient support to promote high atomic dispersion of the active phase – and their application as catalysts in the conversion of sucrose, glucose, fructose and dihydroxyactone to lactic acid and alkyl lactates.

Hydrothermal Conversion of Digested Waste Water Sludge from Biogas Plant to Valuable Components

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With sewage sludge being an abundant biobased resource, the need to utilize this resource is pressing, and being the focus area in many research groups.[1-2] This project uses non-dried digested sewage sludge (DSS) from anaerobic digestion to produce bio-Kjøloil. The process used is hydrothermal liquefaction (HTL) in which the feedstock is heated and pressurized with a reaction medium and formic acid. This is performed both in a reactor of 25 mL and a larger one of 5.3 L. Screening processes are performed to gain knowledge regarding which factors contribute to a higher oil yield and / or better specifications of the oil itself. Oil yields of up to 73 % based on a dry, ash free (*daf*) basis have been obtained, with an energy recovery of up to 94 %. The oils contain compounds relevant for further utilization, such as fatty acids, phenols and glycols.

Figure 1. Oils produced in 25 mL reactor

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Reactive Deep Eutectic Solvents (RDESs): a new tool for Phospholipase D-catalyzed preparation of polar head modified phospholipids

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Recently, the investigation of new biocatalytic strategies as well as the utilization of greener solvents for the chemical modification of organic materials has become a fundamental topic aiming to achieve Sustainable Development Goals.

To this end, the preparation of polar-head modified phospholipids (PLs) with phospholipase D (PLD)-catalyzed biotransformation using Deep Eutectic Solvents (DES) as solvents has been studied. In particular, DESs represent a valid greener alternative solvent to the most common organic ones, perfectly fitting the demand for an environmental sustainable research. PLs constitute the major components of all biological membranes and, thanks to their amphiphilic structure, they are a suitable topic for many areas of biomedical research and for several industrial applications as surfactant, stabilizers and detergents. In particular, the biological activity of PLs mainly depends on the chemical identity of the polar head. For this reason, the modification of PLs polar head for specific applications is of fundamental importance. [1]

In this work, phosphatidylcholine (PC), one of the most abundant PL present in nature, has been transphosphatidylated by PLD using a new reaction media composed by mixtures of DESs and buffer. PC is highly soluble in this new media, avoiding the use of other toxic organic solvents, which were usually necessary in these bioconversions, and the products are easily recovered by precipitation. [2] Moreover, DES acts also as nucleophilic reactant, not only as media, and it inhibits the secondary hydrolysis side-reaction.
The presented results appeared to pave the way to the development of further studies on DES-mediated PLs preparations in a sustainable perspective.

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Selective oxidative cleavage of C-C double bonds by hydrogen peroxide

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Selective oxidative cleavage of unsaturated bonds such as carbon–carbon double bonds is a synthetically important reaction to introduce oxygen functionality into molecules or to degrade complex compounds, especially those from natural sources and biomass. The production of aromatic compounds from biomass resources could provide a sustainable alternative to conventional methods. Thus, oxidative cleavage of olefins represents one of the most important reactions in organic chemistry. It is also a very fundamental reaction in industrial organic synthesis, as it can provide several important products, such as vanillin, benzaldehydes, and aromatic carboxylic acids [1,2].

The standard methods for the conversion of cinnamic acid derivatives into corresponding carboxylic acids are oxidation with Oxone, *m*-CPBA, $NaClO_2$, PIDA, O_2 and H_2O_2/OsO_4. The same reaction is also used for the conversion of ferulic acid to vanillin, where various microorganisms (bacteria, microbial strains, fungal strains, enzymes, etc.), metal oxide catalysts, TiO_2, WO_3-loaded TiO_2 are used [3].

Herein, we have developed general methods for the conversion of cinnamic acid related compounds to corresponding aromatic benzaldehydes, benzoquinones, or aromatic carboxylic acids. The reaction of oxidative cleavage of the carbon-carbon double bond takes place under mild reaction conditions with the green and environmentally friendly oxidant hydrogen peroxide. The choice of solvent significantly influences the course of the reaction. The process also offers a simple and cost-effective alternative for the conversion of ferulic acid to vanillin in high yield. The process was extended to conversion of lignin to vanillin.

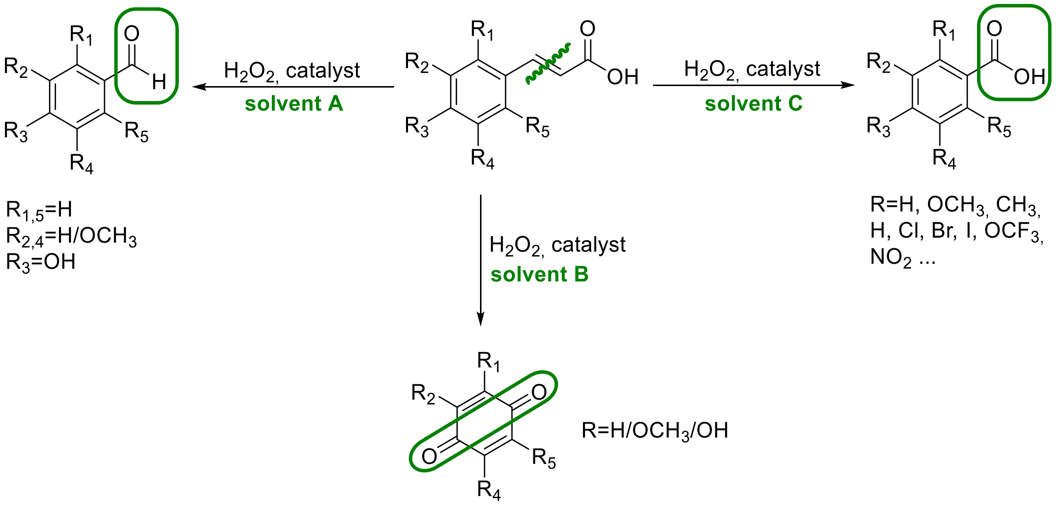

Figure 1. Oxidative cleavage of the C-C double bond of cinnamic acid and related compounds.

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Pillararene-Based PES blended polymers: Design, Preparation and Sustainable Applications

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Nowadays the impact of the anthropological activities on the environment, ecosystem, and human health is seriously increasing. Due to the growth of the global population, it is essential to develop new eco-friendly and sustainable technologies to prevent and remediate the environmental pollution. One of the most challenging tasks of the 21st century is also to face with new emerging pollutants like organic dyes that are widely used in textiles, leather, paper, plastic and cosmetic industries, which represent a threat to the human health for their chemical persistence and toxicity [1]. For their remediation, conventional wastewater treatment methods are not quite efficient, so new advanced filtration systems and techniques have been developed [2].

In this regard, nano- and ultrafiltration hybrid membranes represent a valuable solution for water purification. In particular membranes based on polyethersulfone (PES) are already employed for the removal of different contaminants in ultrafiltration processes, thanks to its thermal and chemical stability. PES is also used as an embedding polymer for the production of new functional membranes to improve their hydrophilicity, porosity, surface properties and adsorption performances, by blending with other polymers, cross-linkers or nanofillers [3].

PDMAEMA, poly[2-(dimethylamino)ethylmethacrylate], is a smart polymer (i.e., capable of adapting and reacting to the surroundings) sensitive to external stimuli such as temperature, pH and ionic strength, with applications ranging from therapeutic and biomedical fields to nanotechnology. For this purpose, this stimuli-responsive polymer [4] could be employed as a useful additive for the production of conjugated PES blends and therefore new advanced membranes.

In this communication it will be shown the production of new polymeric blends, obtained by the combination of PES with synthetized innovative smart polymers, featuring the responsiveness of PDMAEMA polymer and the host-guest properties of the covalently linked pillararenes [5]. New blended membranes and beads, developed for the selective separation of organic dyes in wastewater treatment, are fabricated by a traditional non-solvent induced phase separation (NIPS) process. Finally, preliminary adsorption tests of organic dyes of all the synthesized precursors and polymers are reported.

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Design and development of anti-fouling eco-friendly coatings for marine applications

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Due to the EU limitations involved in the use of biocides in antifouling (AF) marine systems, several technologies have been developed to produce new coatings aimed to interfere directly with the adhesion of microorganism as a result of topography or surface chemistry. It is well known that coatings based on suitable silanes provide an efficient approach for the hydrophobic and antifouling treatment of surfaces. The present work was aimed to give an overview of recently developed sol-gel based AF multicomponent solutions. In any case the synthetic approach was to create an embedding hosting matrix obtained using the sol-gel technique, by reaction of base alkoxysilane precursors (3Glycidyl-oxypropyl-trimethoxysilane, GPTMS = G; 3Amino-propyl-triethoxysilane, APTES = A; Tetraethylorthosilicate, TEOS = T), in the presence of suitable functional molecules or fillers.

In this regards, the reaction with suitable aliphatic derivatives with different lengths of the alkyl chain (Triethoxy-octylsilane, C8; Hexadecyltrimethoxysilane, C16), either fluorinated (Glycidyl-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9, hexadecafluorononylether, F16; Trifluorobutyl-trimethoxysilane, F3) will led to the development of efficient hydrophobic and Fouling Release (FR)coatings (topcoat). Otherwise the reaction performed in presence of inorganic biocidal agents (e.g. derivatives of Zn) and natural functional component (fatty or phenolic acids)iscapable of carrying out a valuable antifouling or antioxidant activity. Application protocols have been optimized to achieve the better adhesion to the substrate and performance, taking into account uniformity and ease of application, and drying time. In some case (i.e. with aliphatic derivatives as additive) the hydrophobic behavior of functionalized top coat is enhanced by introducing an intermediate tiecoat layer with the primer, further decreasing the overall coating wettability, and making them suitable candidates for the development of FR paints. Finally, bacterial adhesion tests and microbiological experiments, carried out in different conditions, were useful to demonstrate that the newly prepared AF and FR coatings are efficient in order to reduce the rate of bacterial adhesion and growth through antifouling/fouling release mechanism.

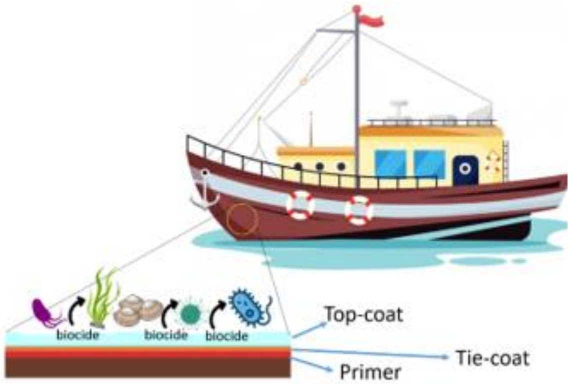

Figure. Antifouling paintings action scheme.

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Development of hybrid geopolymeric-based materials suitable for building sector

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In recent years, new synthetic materials have attracted the interest of many researchers with the aim of developing and promoting their application as protective coatings and structural consolidants for many substrates in construction sector, such as, ceramic, concrete wall, textiles and paintings. To this regard, the scientific community pays the attention on new geopolymer - based hybrid compounds, in order to design innovative materials with better chemical resistance, durability and mechanical characteristics. From a chemical point of view, geopolymers are amorphous inorganic materials similar to ceramics with an aluminosilicate base obtained through a polymerization process, called geopolymerization or geosynthesis, produced starting from natural or waste materials with a high content of aluminum or silicon, such as blast furnace slags of steelworks, clays and fly or volcanic ashes [1]. These materials are featured by low rheological properties, which make them almost unsuitable in restoration works mostly of vertical buildings. For this reason, scientists have recently tried to improve their chemical, physical and mechanical properties by designing hybrid organic - inorganic systems. These novel materials are synthesized by means of a cross-link reaction that occurs between the inorganic phase of the geopolymeric matrix and the organic one featured by an organic compound, such as polysiloxane oligomers, alcoxysilane agents or epoxy resin precursors [2]. This functionalization process improves the performance of the system, as it allows an increase in the viscosity of the mixture, making the hybrid material more versatile in architectural and renovation of buildings [3]. The synthesis scheme takes place via the sol – gel method, which is an eco-friendly approach to functionalize geopolymers, without high temperature treatments, in accordance with green chemistry principles [4]. The research work concerns the modification of the geopolymer matrix at the chemical and nanostructural level, through the condensation process in alkaline conditions, by using alkoxysilane and polysiloxane agents for the implementation of their properties. Their chemical properties, together with the precursor ones, are studied by using X-ray diffraction investigations.

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Picolinium-based Eutectic Systems (ESs) in the Lubrication of Silicon Surfaces

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Eutectic systems (ESs) have recently been proposed as “green” alternatives to mineral oils and ionic liquids (ILs) in the lubrication of several surfaces.[1,2] ESs have similar physical properties to ILs but have the advantage of being cheaper and easier to prepare. In a previous work, we have synthesized sulphur-containing ESs that showed very interesting lubrication properties.[3] Herein, new picolinium salts-based DESs were prepared and tested in the lubrication of silicon surfaces which are relevant for nano/microelectromechanical systems (NEMS/MEMS). All prepared ESs were characterized in terms of their water content, viscosity, wettability and tribological properties. The friction coefficients were measured using steel spheres against Si surfaces. The most promissory ESs showed a good tribological performance, both in terms of friction and wear reduction comparing to commercial lubricants.

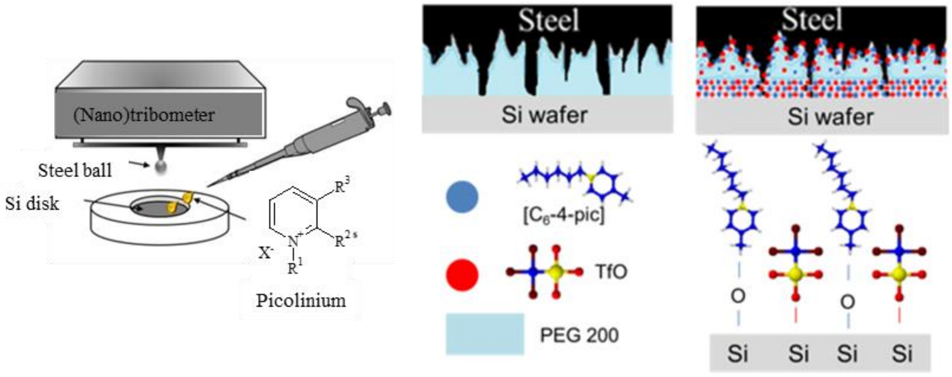

Figure 2. Schematic representation of the (nano)tribometer system and the interactions between the DESs and the Si surface.

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Synthesis and Characterization of Novel Ionic Liquid Crystals-based on Substituted Pyridinium Cations

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Ionic liquid crystals are ordered soft materials containing cations and anions. As they combine characteristics of both liquid crystals and ionic liquids, it is possible to tune their physicochemical and self-assembling properties by selecting specific moieties, allowing to design new functional materials [1]. In this work, several pyridinium bromide derivatives were synthesized based on pyridinium and 2-, 3- or 4- methylpyridinium cations substituted with a dodecyl chain, [C_{12}-n-Pic][Br]. It is known that the rigidity of the cation linked to the flexibility of the alkyl moiety are main requirements for the formation of ionic liquid crystals [2]. In order to evaluate the effect of the alkyl chain length, [C_6-2-Pic][Br] and [C_{16}-2-Pic][Br] were also prepared. Microwave-assisted reactions, as a sustainable approach, were performed to reduce the reaction time, the solvent usage and to improve their yields. All compounds were characterized by spectroscopic techniques (^{1}H and ^{13}C-NMR; ATR-FTIR); thermal analysis (Differential Scanning Calorimetry); Polarized Optical Microscope and X-Ray Powder Diffraction. The results obtained indicate the formation of thermally induced smectic phases. The insertion of a methyl group in *meta* and *para* positions of the pyridinium ring significantly reduces the clearing point and the liquid crystalline range, when compared with the parent [C_{12}Pyr][Br] and the *ortho*-substituted. Moreover, [C_{12}Pyr][Br] was further investigated by Dielectric Relaxation Spectroscopy.

Acknowledgments

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Isocyanide-bases One-Pot Synthesis of Thiocarbamates

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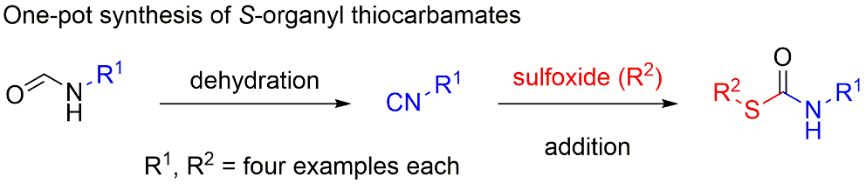
An efficient isocyanide-based synthesis of *S*-thiocarbamates was discovered and thoroughly investigated. The new reaction protocol is one-pot and allows the direct conversion of *N*-formamides into thiocarbamates by initial dehydration with *p*-toluene sulfonyl chloride to the respective isocyanide,[1] and subsequent addition of a sulfoxide component. Contrary to recent literature, which also relies on isocyanides as starting material,[2-5] in this protocol, no isolation and purification of the isocyanide component is necessary, thus significantly decreasing the environmental and financial impact of the synthesis. The protocol was applied to synthesize a library of sixteen thiocarbamates utilizing four *N*-formamides and four commercially available sulfoxides. Furthermore, experiments were conducted to investigate the reaction mechanism. Finally, four norbornene-based thiocarbamate monomers were prepared and applied in controlled ring-opening metathesis polymerization (ROMP) reactions. The polymers were characterized *via* size-exclusion chromatography (SEC) and their properties were investigated utilizing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to establish possible applications in material sciences.



Scheme 1. One-pot procedure toward *S*-organyl thiocarbamates. The isocyanide component is directly converted into its respective thiocarbamate without previous purification.

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Development of a low environmental impact couple of solvent and catalyst for Nenitzescu reaction

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Indole is an important core in many biogenic compounds such as tryptophan, serotonin, melatonin and many other hormones, alkaloids and secondary metabolites. The reaction discovered by Costin Nenitzescu in 1929[1] is attractive when a 5-hydroxyindole is needed, because the reactants are enamines and quinones, cheap and simple starting materials. Major advancements in this reaction have been done by the group of Velezheva[2], that developed the application of mild Lewis acids, such as zinc chloride, to perform the reaction in dichloromethane. In the context of reduction of environmental impact, we aimed to substitute dichloromethane and zinc with less toxic and polluting solvents and catalysts to find that cyclopentyl methyl ether (CPME) is an effective solvent for this synthesis at room temperature and magnesium salts can provide yields comparable to zinc for a few substrates. The reaction is fast, run at room temperature and the work-up consists of a simple filtration; this, altogether with the high recyclability of CPME contributes to an overall reduction of waste and energy consumption.

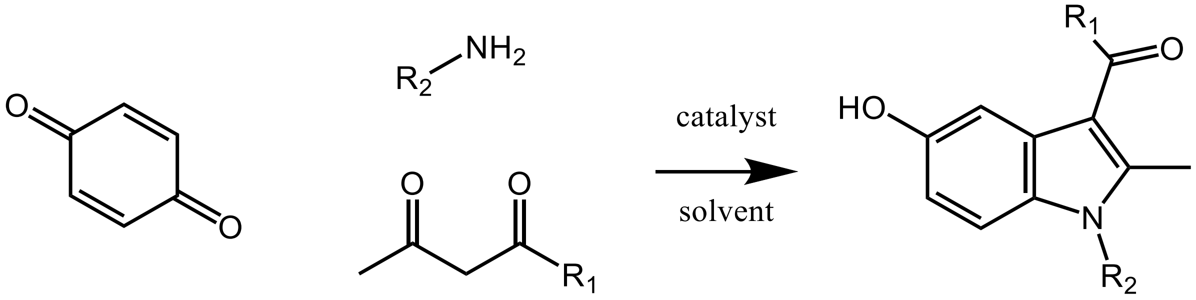

Figure 1. 5-hydroxyindoles synthesis catalyzed by Lewis acid.

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Levulinic Acid Hydrogenation to γ-valerolactone over Single Ru Atoms on TiO_2@Nitrogen Doped Carbon Support

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The transformation of levulinic acid (LA) to γ-valerolactone (GVL) in water at room temperature is very interesting. In this work, we designed and prepared single Ru atoms on TiO_2@nitrogen droped porous carbon support catalyst (Ru/TiO_2@CN). It was demonstrated that the catalyst had very high activity, selectivity and stability for the conversion of LA into GVL at room temperature in water. The turnover frequency (TOF) could reach 278$mol_{GVL}mol_{Ru}^{-1}$ h^{-1} at complete conversion, which was about 35 times higher than that of the commercial Ru/C. In addition, only GVL was generated in the reaction over the catalyst of this work.

Table 1. Catalytic Performance of Ruthenium in the hydrogenation of LA[a]

Entry	Catalysts	Catalyst (mg)	S/M[b]	Time (h)	Conv. (%)	Selectivity (%)		TOF[d] mol_{GVL} g_{Ru}^{-1} h^{-1}
						GVL	Others[c]	
1[e]	Ru/TiO_2@CN	10	3610	8	78	100	0	234
2	Ru/TiO_2@CN	10	3610	12	95	100	0	285
3	Ru/TiO_2@CN	10	3610	13	100	100	0	278
4	Ru/TiO_2@C	10	2021	12	83	99	1	141
5	Ru/TiO_2@CN-500	10	3887	12	-	-	-	-
6	Ru/TiO_2@CN-900	10	2197	12	3	100	0	6
7	Ru/TiO_2	10	4211	12	13	100	0	10.5
8	TiO_2@CN	10	-	12	-	-	-	-
9[f]	Ru/TiO_2@CN	10	3610	12	40	89	11	-
10[g]	Ru/TiO_2@CN	10	3610	12	66	86	14	-
11[h]	Ru/TiO_2@CN	10	3610	12	2	100	-	-
12[i]	Ru/C	10	101	12	100	94	6	7.91
13[j]	PtO_2	400	286	44	87	-	-	6.5
14[k]	Ru/FLG	15	1460	8	99.3	97.7	2.3	178
15[l]	Ru/C	250	348	50	100	97.5	2.5	6.8

[a] Reaction conditions: LA (0.5 mmol), H_2O (1 mL), 30 °C, H_2 (6 MPa). [b] S/M is the molar ratio of substrate (LA) to active metal (Ru). [c] Other by products include γ-hydroxyvaleric acid, angelica lactone and other unknown products. [d] Turnover Frequency (TOF) of GVL = moles of produced GVL)/(mass of Ru)(reaction time), $mol_{GVL}g_{Ru}^{-1}$ h^{-1}. [e] H_2, 4 MPa, 20°C. [f] Methanol. [g] Ethanol. [h] 1, 4-Dioxane. [i] 5% Ru/C. [j] Reaction conditions in the literature 1: 500 mmol LA, 0.4 g PtO_2, 150 mL ethyl acetate, room temperature, 2.3-3.0 bar H_2, 44 h. [k] Reaction conditions in the literature 2: 4.3 mmol LA, 2% Ru/FLG (few-layer graphene), 10 mL H_2O, 4 Mpa H_2, 20 °C. [l] Reaction conditions in Ref 3(43 mmol LA, 5% Ru/C, 25 °C, 12 bar H_2, 50 h).

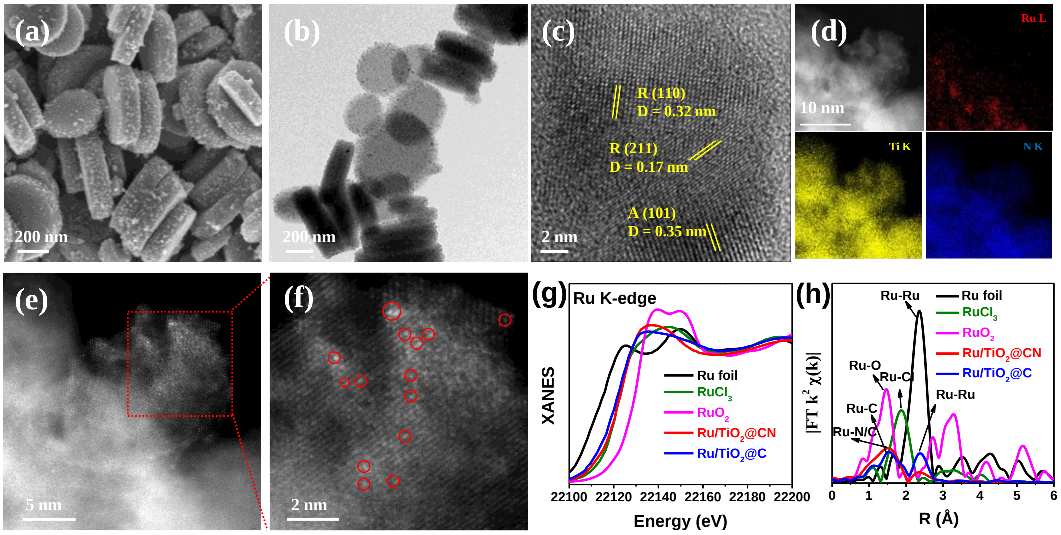

Figure 2. Structural characterizations of the Ru/TiO_2@CN catalyst: (a) SEM image; (b and c) TEM images; (d) HAADF-STEM image and corresponding element maps for Ru (red), Ti (yellow) and N (blue); (e and f) HAADF-STEM and enlarged images of the Ru/TiO_2@CN catalyst, with single Ru atoms highlighted by red circles; (g) XANES spectra of Ru/TiO_2@CN and Ru/TiO_2@C for Ru K-edge. (h) Fourier transformed (FT) k^2-weighted $\chi(k)$-function of the EXAFS spectra for Ru K-edge.

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Base and Acid Free copper catalysed C-H ammination

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Cross dehydrogenative coupling reactions are a tool of great importance in synthetic organic chemistry, allowing the direct functionalization of C-H bonds with the aid of a stoichiometric oxidant to achieve C-C and C-heteroatom bonding. The wide variety of available reactants with C-H bonds make this new field of study potentially very versatile.[1]

Affordability, versatility, low toxicity and abundance are the main factors that make copper-based catalysts so desirable for organic chemistry. The versatility of copper is mainly due to its ability to transfer one or two electrons. For this reason organic transformations, such as oxidation and reduction, gain particular advantage by the use of copper catalysis.

Several procedures exist for the copper-catalysed direct amination of azoles: major drawbacks include the use of oxygen, the need to use a large excess of amine, low azole substrate versatility and, lastly, acidic or basic conditions.[2]

The aim of the present work was to optimise a ligandless, acid- and base-free procedure in ambient air, to demonstrate its applicability to a wide range of amines and to investigate the effect of ultrasounds on these reactions. Moderate results were obtained using CuCl as catalyst, relatively mild heating and, most importantly, without the need of ligand or acid/base additives.

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Flash Vacuum Pyrolysis as a Green, Solvent–Free Technology

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Flash vacuum pyrolysis (FVP) – a special form of gas-phase thermolysis – is a synthetic methodology in the absence of a solvent and reagents ("chemistry without reagents").[1] Secondary reactions are thus diminished and usually intramolecular transformations such as eliminations, rearrangements or cyclizations occur upon FVP thermolysis. Reactions performed under FVP conditions are generally clean, convenient and efficient, and can be considered as highly atom economic and waste minimizing. FVP is mostly used for reaction discovery and the synthesis of heterocyclic compounds, which cannot be easily obtained by other methods.

Herein, we present a study on the regioselectivity of the Gould-Jacobs cyclization reaction of compound **1** using different thermal activation methods in the gaseous or liquid phase (Figure 1).[2] Under FVP conditions (up to 800 °C and 10^{-3} mbar) very short reaction times (~1 ms) can be achieved, which enabled the generation of the kinetic pyrido pyrimidinone product.

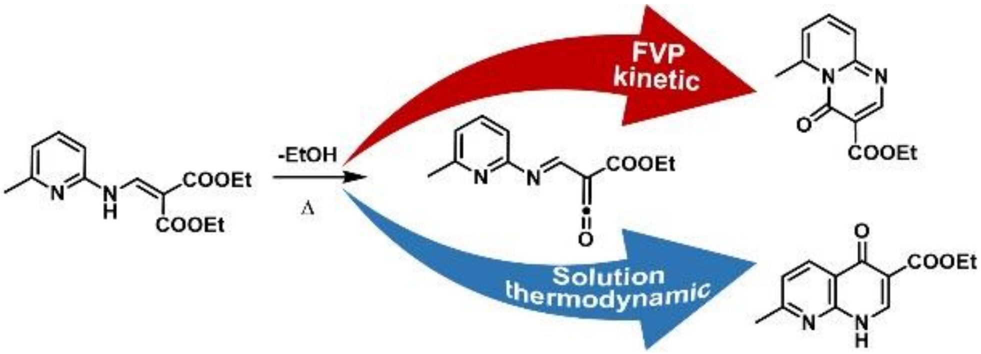

Figure 1. Regioselectivity of the Gould-Jacobs reaction.

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3. ENERGY SAVING

Design of Efficient, Stable and Lead Free Perovskite Solar Cells

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The past 10 years have witnessed exciting developments in the field of Perovskite Solar Cells (PSCs). Recent research in the field has reported on high efficiency devices demonstrating a power conversion efficiency of around 25.5% (NREL certified) [1]. This exceeds the efficiency of most extensively commercialized silicon based solar cells, which ranges between 12% to 16%. Furthermore, the fact that PSCs can be produced via less complex solution processing methods using a variety of abundant, readily available raw materials makes this technology very promising as the future for both commercial and domestic solar energy harvesting systems [2, 3]. However, a number of outstanding issues are yet to be addressed before practical, commercial PSCs can be launched into the market. The major challenge is that PSCs developed to date have poor stability that limits their operational life to just about 10 000 hours under simulated operating conditions in the laboratory at 0% loss in efficiency [4]. This falls short of the 20years plus which, silicon solar cells have demonstrated under real world conditions. The other challenge is that the highly efficient PSCs are made based on perovskite films that contain toxic lead (Pb) [5]. The perovskite films can easily degrade under environmental stressing and release Pb creating an environmental hazard.

In this current work, studies aimed at developing improved perovskite films that are less susceptible to degradation under environmental stressing and that do not contain toxic Pb are being conducted. Studies conducted so far point towards a solution where computational modeling can be applied to screen for materials that can substitute Pb based perovskite films, while maintaining comparable structural consistency to preserve already obtained efficiency levels [6]. We propose reduced dimensional perovskites by inducing chirality into the structure using organic ligands [7].

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Co–Cu Bimetallic Metal Organic Framework Catalyst Outperforms the Pt/C Benchmark for Oxygen Reduction

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Platinum (Pt)-based-nanomaterials are currently the most successful catalysts for the oxygen reduction reaction (ORR) in electrochemical energy conversion devices such as fuel cells and metal-air batteries. Nonetheless, Pt catalysts have serious drawbacks, including low abundance in nature, sluggish kinetics, and very high costs, which limit their practical applications. Herein, we report the first rationally designed nonprecious Co–Cu bimetallic metal–organic framework (MOF) using a low-temperature hydrothermal method that outperforms the electrocatalytic activity of Pt/C for ORR in alkaline environments. The MOF catalyst surpassed the ORR performance of Pt/C, exhibiting an onset potential of 1.06 V vs RHE, a half-wave potential of 0.95 V vs RHE, and a higher electrochemical stability ($\Delta E1/2 = 30$ mV) after 1000 ORR cycles in 0.1 M NaOH. Additionally, it outperformed Pt/C in terms of power density and cyclability in zinc-air batteries. This outstanding behavior was attributed to the unique electronic synergy of the Co−Cu bimetallic centers in the MOF network, which was revealed by XPS and PDOS.

Table 1. Calculated Adsorption Energies of OH and O2 and Formation Energies of OOH and O on Co and Cu Sites

(A) Adsorbates	Adsorption Energy (EV)		(B) Species	Formation Energy (EV)	
	On Co	On Cu		On Co	On Cu
OH	-1.125	-1.129	OOH	-2.45	-2.17
O_2	-0.394	-0.192	O	0.36	0.62

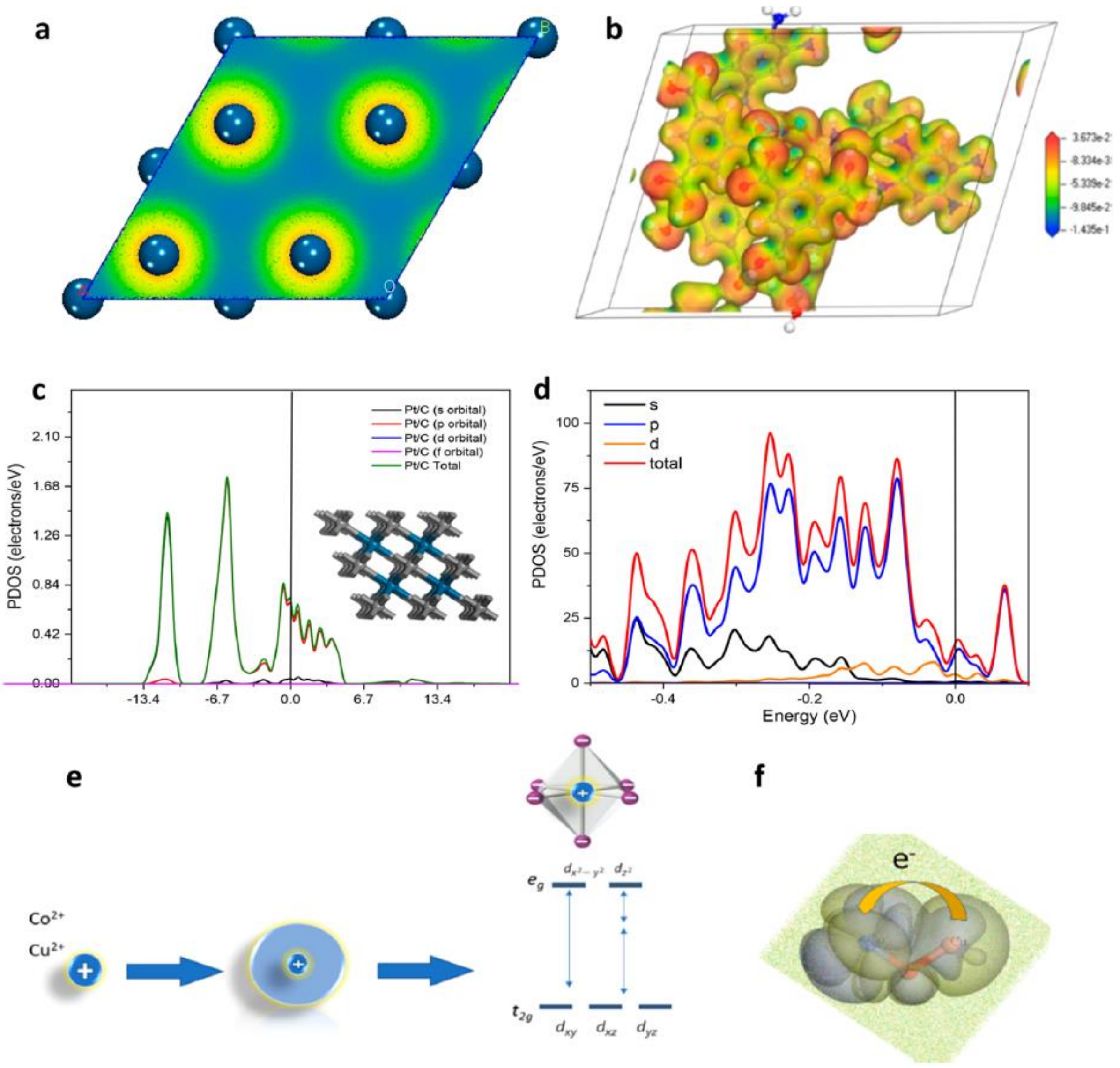

Figure 3. DFT calculations. The electron density distribution of (a) Pt/C and (b) BTC-Co-O-Cu-BTA MOF. The density of states of (c) Pt/C and (d) BTC-Co-O-Cu-BTA MOF. (e) Octahedral order of six negative charges around a metal ion complex. (f) Charge transfer direction in the Co−Cu bimetallic MOF clusters.

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Photocatalytic H_2 production from H_2S decomposition

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Photocatalytic hydrogen production by H_2S splitting offers sustainable energy generation and abatement of environmental pollution, which is energetically more favorable than photocatalytic water splitting [1]. Sulfide-based materials, as photocatalysts, are regarded as good candidates for H_2 evolution due to their excellent solar spectrum response and high photocatalytic activity [2].

In our research, we focused on the use of CdS-ZnS composite because of its controllable band gap and excellent performance for H_2 evolution under visible light [3]. We mainly investigated the effect of several parameters on the H_2 production activity of this type of photocatalysts in order to obtain a cost-effective material.

The CdS-ZnS composite with an enhanced photocatalytic activity for H_2 production was synthesized from ammine complexes. The illuminations were performed using simple LED lamps and the effects of the ammonia content, the hydrothermal treatment and the washing of the catalyst were investigated. It was shown that the initial pH of preparation and the temperature of hydrothermal treatment did not affect the performance of CdS-ZnS. However, the ammonia content was proven to highly influence the rate of H_2 production in this system and so XRD measurements were performed to explain this dependence.

The excellent photoactivity of the CdS-ZnS catalysts for hydrogen generation encourages further investigations to enhance its performance by optimization of the reaction conditions.

Table 1. The rate of H_2 production (ml/h) as a function of the ammonia content

Ammonia content	Ø	Stoichiometric amount	Excess
Rate of H_2 production	3.7 ml/h	8.1 ml/h	6.3 ml/h

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Next generation of green OPV cells based on water-soluble photo-active material

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In recent years, alternative energy sources have been studied to avoid the decrease of fossil sources. In particular the attention has been focused on exploitation of solar energy by the development of organic photovoltaic solar cells (OPVs) based on polymeric photoactive layers. With the aim to make this possible at sustainable costs using eco-friendly techniques and maintaining final excellent intrinsic optoelectronic properties, research has prompted towards photovoltaic technologies based on water/alcohol-soluble conjugated polymeric solar cells (WSCPs).[1]

For this purpose, a solar cell based on a water-processable single material has been prepared (Figure 1). In detail, the ionic water-soluble poly[3-(6-tributylphosphonium)thiophene-*co*-3-(6-fullerenylhexyl)thiophene] (P[(T6buP$^+$)-*co*-(T6F)]) has been obtained through two different post-functionalization of the regioregular polymeric precursor poly[3-(6-bromohexyl)thiophene] (PT6Br).[2]

The final double-cable copolymer has been characterized by nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR), thermal analysis (TGA), morphological analyses (FE-SEM, AFM) and UV-Vis spectroscopy in order to evaluate its main characteristics. The polymeric derivative showed a thermal stability suitable for the final application combined with a good solubility in green polar solvents, i.e. water and alcohols, and a low tendency to form aggregates in solid state. Finally, it has been tested as photoactive layer in a OPV device, using methanol as filming solvent. The obtained photo-conversion efficiency (PCE = 3.11%) indicates that the prepared thiophene copolymer is very promising for applications in green polymeric solar cells.

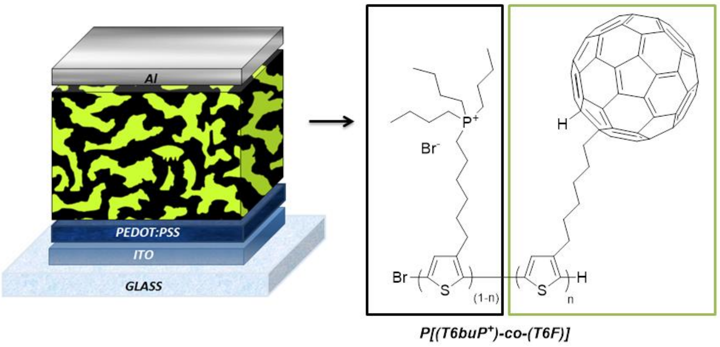

Figure 1. Structure of WSPCs based on copolymer synthetized.

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Interaction of [NiFe] hydrogenases on a graphite electrode

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Hydrogenases are a family of enzymes that have been studied by researchers in renewable energies in the last years, due their ability of catalyze the redox reaction of hydrogen:

$$2H^+ + 2e^- \leftrightarrow H_2$$

This reaction indicates that hydrogenases could be used to produce hydrogen or electricity in electrochemical devices. Some studies have tried of immobilize these enzymes on the surfaces of electrodes with some grade of successful [1], but better understanding of how this process occurs at atomic level is necessary, because the orientation of the enzyme with respect to the electrode´s surface is very important in order to ensure a good flux of electrons to the catalytic center of the enzyme. In order to determine such orientation, computational simulations based on the Poisson-Boltzmann equation, in an implicit-solvent model were used to calculated the total energy of the interaction of the hydrogenase 1e3d (pdb code) on a graphite electrode using the PyGBe software[2]. Considering as independent variables the pH, salinity and the electric potential.

The preliminary results suggest that the orientation of the enzyme can be manipulated modifying the pH, and the electric potential applied to the electrode. According to our preliminary results, the best positions are obtained at pH 6 and 8 with an electric potential of 0.05 V, because under these conditions the external iron-sulfur cluster is orientated towards the surface of the electrode. This could favor the transfer of the electrons to the catalytic center and for therefore the redox reaction of hydrogen.

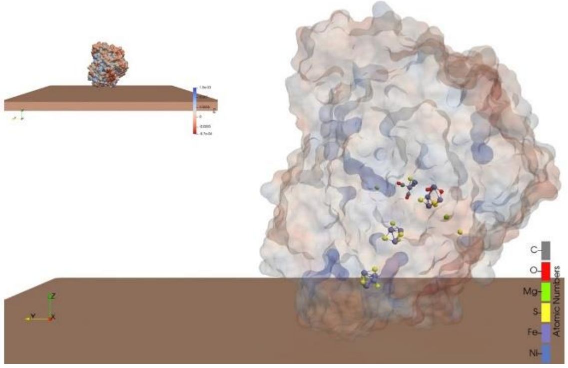

Figure 1. Hydrogenase (1e3d), orientated on the surface of the electrode at pH 6, and electric potential of 0.05 V, the colored atoms indicate the metallic clusters.

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4. FOOD SAFETY

Photocatalytic degradation of fungicide difenoconazole via photo-Fenton process using α-Fe_2O_3

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Nowadays, Human consumption leads to massive industrial sector manufacturing. Pesticides are one of the most toxic chemicals widely used to increase agricultural production. Those compounds present several threats to the environment. The photodegradation of difenoconazole (DFL) fungicide was carried out via Photo-Fenton process using synthesized α-Fe_2O_3 nanoparticles. The α-Fe_2O_3 was prepared using hydrothermal approach at 180°C with ferric chloride and sodium hydroxide reagents. The sample was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman analysis. Average crystallite size has been recorded to be 27nm and the surface area was found to be S_{Bet}=24.82 m^2/g. DFL removal has been tested under divers systems: UV photolysis, UV/H_2O_2, UV/α-Fe_2O_3, Fenton and Photo-Fenton process. The kinetic has been been monitored using High-Performance Liquid Chromatography (HPLC). All irradiation tests were achieved at 254 nm using UVC Lamp. An optimization of reaction conditions (pH, oxidant concentration, and catalyst dosage) were performed As a result, it was demonstrated that Photo-Fenton process (UV/ α-Fe_2O_3/H_2O_2) as most effective for DFL removal. The optimal catalyst dose of α-Fe_2O_3 for high removal rate is about 0.5g/l at initial solution pH. The mineralization efficiency attained 83.67%. The oxidation kinetics of DFL was recorded to accord with the pseudo-first order kinetic model. Finally, a possible mechanism pathway was proposed based on detected intermediates using gas chromatography-mass spectrometry (GC-MS) analysis.

Keywords: Definoconazole, Photocatalysis, Photo-Fenton, Hematite, wastewater treatment.

Development of green methodologies in the chemical research of by-products and wastes from coffee crops and coffee processing.

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The agrifood industry generates a series of by-products with harmful environmental and economic impacts[1]. Coffee beans are one of the most important food commodities in the world, with an estimated 10.5 million tons of by-products or wastes generated by the 2020/2021 coffee harvest alone[2]. Their current destination does not add sufficient value to the production chain or are potentially harmful to the environment. The presence of bioactive compounds in these waste materials may open opportunities for their uses in a biorefinery approach. This work presents the most wide-ranging chemical investigation of fourteen coffee by-products collected from farms to factories, as well as a wide selection of alternative green solvents for extracting bioactive metabolites from them. For this purpose, (i) a comprehensive two-phase extraction (EtOH-H_2O and n-heptane) was developed and all extracts were analyzed by Ultra-high-performance liquid chromatography coupled to UV/Vis and time-of-flight mass spectrometry (UHPLC-PAD/UV-ESI-QTOF-MS/MS), and Gas chromatography coupled to mass spectrometry (GC-MS); (ii) Four by-products were statistically selected for further investigation with seventeen different alternative green solvents, including hydrophilic and hydrophobic Natural Deep Eutectic Solvents (NADES) and their extraction selectivities were compared side-by-side using UHPLC-PAD/UV and GC-MS; (iii) Greenness assessments of such extractions were achieved using multi-parametric metric and compared to reference methods. As a result, forty-two compounds were found for the first time in coffee by-products, including the bioactive neomangiferin, Kaempferol-3-O-rutinoside, Lup-20(29)-en-3-one and 3,4–dimethoxycinnamic acid. In addition, five by-products generated inside a factory had caffeine (53.0-17.0 $mg.g^{-1}$) and/or chlorogenic acid (72.9-10.9 $mg.g^{-1}$) contents comparable to coffee beans (the commodity), while another three samples collected in farms presented considerable amounts of these bioactive compounds (16.5-6.8 and 38.9-0.8 $mg.g^{-1}$, respectively). Regarding alternative green solvents, the highest levels of caffeine (41.6-13.0 and 37.8-14.5 $mg.g^{-1}$) and chlorogenic acid (78.7-2.7 and 58.3-3.3 $mg.g^{-1}$) contents were obtained using Choline chloride:Sorbitol (4:1) and Choline chloride:Lactic acid:Water (1:2:2), respectively. On the other hand, hydrophobic NADES led to the extraction of a different set of compounds from the same matrix, such as sterols, monoacylglycerols and fatty acids. Such by-products are a source of a range of bioactive compounds and could be explored with potential economic and certainly environmental benefits.

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A green approach to valorize soy agro by-products

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Soybean is the major oilseed crop worldwide, however, its vast production has been leaving by-products behind that could be valorized considering their composition in high-added compounds. It is estimated that 597 million metric tonnes of branches, leaves, pods, and roots will be left on the ground in soybean post-harvesting in 2020/21 [1,2]. These underused soy parts are sources of bioactive compounds, such as fatty acids, saponins, flavonoids, organic acids, and others. First, we investigated soy plant by-products collected just after mechanical harvesting, applying an untargeted metabolomics approach. A two-liquid-phase dynamic maceration composed of a hydroethanolic and heptane fraction was used to extract a wide range of compounds, and the produced hydroethanolic and heptane extracts were analysed by UHPLC-ESI-QTOF-MS/MS and GC-EI-QTOF-MS, respectively. Second, a green approach combining Natural Deep Eutectic Solvents (NaDES) and Pressurized Liquid Extraction (PLE) has been employed for generating extracts with potential bioactivity properties, such as antioxidant, anti-inflammatory, and anti-neurodegenerative activities.

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Development of a novel UHPLC-MS/MS method for the determination of ochratoxin A in tea. Greenness assessment

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Tea is a traditional beverage widely consumed worlwide. Approximately, because the annual increase in its consumption, near 7 million tons will be produced in 2023. Tea may contain different families of compounds associated to promote human health wellness. However, numerous publications show that also chemical contaminants and natural toxins produced by filamentous fungi (mycotoxins) can be found. Mycotoxins have been detected in different tea varieties (black, red, green), like aflatoxins, ochratoxin A (OTA), and fumonisins. OTA is responsible for producing many effects on human and animal health, such as nephrotoxic, teratogenic, immunosuppressive, embryotoxic, genotoxic, and mutagenic effects. Hence, the European Commission Regulation (EC) 1881/2006 [3] has established maximum levels (MLs) of OTA in foods and feed products (*e.g.*, a 5 ug kg^{-1} MLs has been set for roasted coffee), but no European regulation for mycotoxins in tea samples has been reported yet [1]. In addition, to make compatible detection and regulation limits for mycotoxins analysis, robust and sensitive analytical methods are required. These objectives are attainable only if cutting-edge technology (UHPLC-MS/MS, among others) is applied. The development of sensitive, accurate, low-cost, quick, and eco-friendly method has become a major challenge in the analytical chemistry field, a growing trend related to environmental awareness has emerged in recent years. In this context, the dispersive liquid-liquid microextraction based on the solidification of a floating organic drop (DLLME-SFO) technique satisfies the general characteristics of green strategies. Nowadays, to establish an analytical methodology, not only the overall performance should be considered, but also the greenness assessment through a variety of metrics. Several green metrics can assess sustainability of analytical procedure, among them, the Analytical Eco-Scale, the Green certificate (GC), and the recently introduced Analytical GREEnness calculator (AGREE), are the most reported. In this work, the evaluation of the concentration levels of OTA in tea beverage samples developing extraction and preconcentration steps through the solidification of a floating organic drop combined with an additional octadecyl silane clean-up step is proposed. The obtained extract was analyzed by UHPLC-MS/MS. Interferences from the matrix were effectively reduced and, consequently, recovery increased from 43.18% ± 4.1% to 96.02% ± 2.54%. The validation assays were carried out by external and spiked samples calibration, with satisfactory recoveries. An adequate dynamic calibration range was obtained over a concentration interval between 0.5 and 70 μg mL^{-1} OTA. Capabilities of detection and quantification were 0.5 and 1.4 μg mL^{-1}. Finally, the greenness assessment of the developed methodology was assessed by means of the green certificate, achieving the A performance [2].

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Improving the performance of thin film nanocomposite membrane used for water treatment and desalination

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A thin film nanocomposite (TFN) membrane is widely applied to treat waste and saline water from contaminations. As it is dominating many water purification industries, particularly desalination, developing its properties and enhancing its total performance became crucial. Here, we filled different types of nanomaterials in order to improve the permeate water flux and salt rejection. Although the intrinsic relationship between water flux and salt rejection is the trade-off, some additives showed improvement in the water flux with maintaining the rejection high or even improve it. Different types of Silica (MCM-41 and SBA-15), metal-organic frameworks (MOFs, UiO-66 and MIL-125), and recently MXene were used to improve the membrane's properties. Adding these additives aimed to improve the hydrophilicity, surface area, and provide direct channels for water molecules transportation. It was noticed that MOFs improved the total performance to a higher degree than conventional additives, which was attributed to their exceptional properties, such as high surface area and design. Primary experiments using MXene particles showed a good improvement in water flux without decreasing the salt rejection. Continuous effort is needed to develop new materials that fit well within the membrane's structure and improve the performance. Also, comprehending the transport mechanism that still has a lack is one of the main keys to further improve the properties and operational efficiency.

Sugar-based surfactants: chemoenzymatic synthesis and interfacial properties evaluation

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Sugar Fatty Acid Esters (SFAEs) are a family of non-ionic surfactants widely used as emulsifiers in many market sectors (*i.e.* food and cosmetic industry). These tensides are becoming of great interest because, among other features, they are fully biodegradable and can be produced from renewable resources,[1] such as cheese whey permeate (the main waste stream of the dairy industry). The current industrial synthesis requires harsh reaction conditions which result, in most cases, in complex mixtures. An alternative and more sustainable approach deserves to be investigated. Indeed, SFAEs can be produced through a solvent-free esterification reaction between a modified sugar and a molten fatty acid, catalyzed by a lipase.[2]

Lactose, the main component of whey permeate, was used as the starting material to synthesize butyl-β-D-galactopyranoside through a transglycosylation reaction catalyzed by the immobilized β-galactosidase from *Aspergillus oryzae* in a ternary system composed of *n*-BuOH/acetone/McIlvane buffer 50 mM pH 4.5 (50/30/20).[3] Glucose, the by-product of the transglycosylation reaction, was converted into isomeric mixtures of glucosides by reaction with a number of naturally occurring alcohols in the presence of Amberlyst® 15. Resulting glucosides were submitted to a Novozyme® 435-catalyzed esterification with lauric, palmitic, and stearic acid in a solvent-free system, thus affording a set of SFAEs.

Moreover, the sunflower oil / water interfacial tension (IFT) values by varying the amount of the 6-*O*-lauryl, 6-*O*-palmitoyl and 6-*O*-stearyl-1-*O*-butyl glucosides were measured by a Gibertini tensiometer exploiting the Du Noüy ring method. All the surfactants allowed the IFT reduction from 26 mN m^{-1} (sunflower oil / water interface) to a value around 3 mN m^{-1}, corroborating the actual surface properties of the tested sugar-based molecules.[4]

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5. CLIMATE CHANGE DAMAGES MITIGATION

Adsorptive removal of methylene blue dye from aqueous solution using biodegradable superabsorbent polymer hydrogel and its composites

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Superabsorbent polymers (SAP) are the class of polymeric hydrogels that are cross-linked systems having a unique ability to imbibe water hundred times of their dried weight. Now a days SAP are extensively used for the adsorption of organic and inorganic pollutants. Herein, SAP hydrogel and their composites were prepared, with the incorporation of activated charcoal (SAP-AC) and TiO_2 nanoparticles (SAP-TiO_2). A systematic study on the adsorption properties of the desired adsorbents was conducted for the deep removal of eco-toxic organic dye such as methylene blue (MB). Initial water retention capacity of the prepared SAP was determined by its swelling ratio tests. SAP showed maximum water retention capacity of 578 ± 7 g g^{-1} (grams of water absorbed per gram of dry polymer) followed by SAP-AC and SAP-TiO_2 respectively. A column was mounted and the adsorption parameters were optimized using an experimental Doehlert uniform array design for two variables (temperature, pH), using the response surface methodology (RSM). A continuous up-flow fixed bed column was fed with 300 mL of MB (100 -200 ppm) using a peristaltic pump. About 70 mg of dried composite adsorbent was immersed in the glass tubular reactor with 6 cm internal diameter and 30 cm in length. The adsorption was maintained for 24h time duration and a small sample aliquot (5 mL) was collected at definite time intervals and was analyzed using a UV-Visible spectrophotometer (λ_{max} = 665 nm) for the residual MB concentration. It was observed that the pH and temperature have a marked effect on the MB adsorption and swelling ratio of the composite. In order to find the effect of initial MB concentration, the adsorption of MB was investigated for optimized conditions using higher concentrations in the range of 100 and 200 mg L^{-1} respectively. At initial MB concentration of 100 mg L^{-1} using SAP, the MB adsorption capacity reached 367.09 mg g^{-1} with 88.93% removal efficiency and swelling ratio of 24.03 g g^{-1}, for SAP-AC it attained 399.03 mg g^{-1} with 95.89% removal efficiency and swelling ratio of 265.40 g g^{-1} and for SAP-TiO_2 it achieved 373.95 mg g^{-1} with 93.11% removal efficiency and swelling ratio of 64.15 g g^{-1}. According to the results obtained, when the initial MB concentration was increased to 200 mg L^{-1}, an increase in MB adsorption capacity was observed with a gradual decrease in the percent MB adsorption and swelling ratio as compared to lower MB initial concentrations. Comparatively, using SAP-AC as adsorbent, a higher (736.75 mg g^{-1}) MB adsorption capacity was obtained with 89.74% removal efficiency and the swelling ratio reached the value of 104.00 g g^{-1}, respectively. On the other hand, MB adsorption capacity reached the value of 711.45 mg g^{-1} with 89.65% of MB adsorption percentage and the swelling ratio was 33.98 g g^{-1} correspondingly.

Microwave-driven hydrothermal synthesis of α-Fe_2O_3 nanorings as CeO_2 catalyst support for CO_2 conversion

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Hematite (α-Fe_2O_3), the most common and stable iron oxide allotrope, is abundant in nature and can present several morphologies, depending on the preparation method. The conventional hydrothermal procedure is the most used to prepared nanoring-shaped α-Fe_2O_3. However, prolonged reaction time (48 h), small-scale preparation and the difficult reproducibility of the process are drawbacks for this route. On the other hand, microwave-driven (MW) methods have been used to reduce time and energy in different processes [1]. α-Fe_2O_3 presents interesting properties for batteries, biomedical, magnetic composites and catalysis applications. Thus, this abundant and economic material can be doped or impregnated with a different metal or metal oxides such as CeO_2, which is known as an active catalyst for the direct synthesis of DMC from CO_2 and methanol [2]. Herein, we investigated the potential synergistic effect between CeO_2 catalyst and α-Fe_2O_3 nanorings in the CO_2 conversion as a green and sustainable catalysts for the production of DMC. α-Fe_2O_3 nanorings were prepared by MW-assisted hydrothermal synthesis from $FeCl_3$, NaH_2PO_4, and Na_2SO_4 aqueous solution at 220 °C. $Ce(OH)_3$ was deposited on the surface of the as-prepared α-Fe_2O_3 nanorings by chemical precipitation in different Ce:Fe molar ratios. The samples were centrifuged, dried and calcinated at 400 °C. Catalytic tests were carried out in a 100 mL Parr batch reactor. TEM image of CeFe-11 (Fig. 1) shows the presence of α-Fe_2O_3 nanorings well decorated with CeO_2 nanoparticles. Fig. 2 shows the XRD pattern presenting two crystalline phases: one composed of hematite (PDF 33-0664) and the other corresponding to CeO_2 (JCPDS 34-0394). From Table 1 it can be seen that CeFe-11 presents the best catalytic activity compared to bare CeO_2 and α-Fe_2O_3. This result may be associated with its high surface area (95 m^2/g), which seems essential in the synthesis of DMC. Yet, EPR studies are being conducted to investigate the influence of oxygen vacancies in the material's catalytic performance.

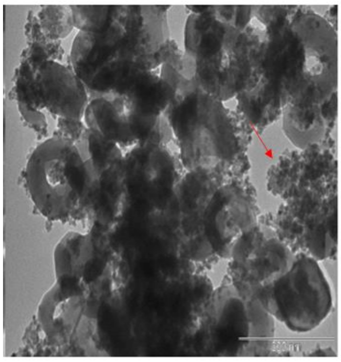

Figure 1. TEM images of the CeFe-11 catalyst.

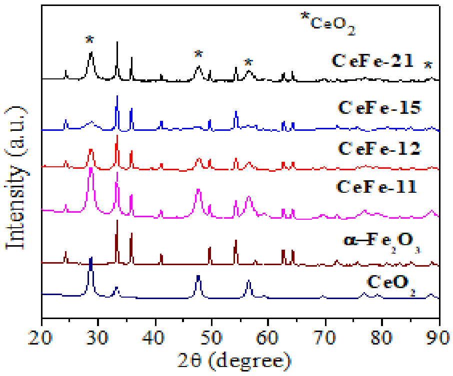

Figure 2. XRD spectra of the all catalysts.

Table 1. Catalytic data of the CeO_2-Fe_2O_3 mixed oxide particles. (50 bar CO_2, 140 °C, 0.1g cat., 3 h).

Catalyst	Molar Ratio	DMC yield[a]	A[b]
CeO_2	0	1.5	60
α-Fe_2O_3	0	1.6	26
CeFe-11	1:1	7.1	95
CeFe-12	1:2	5.0	57
CeFe-15	1:5	2.1	56
CeFe-21	2:1	4.9	50

[a] $mmol_{DMC}/g_{cat}$.
[b] Surface area (m^2/g).

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Pb-Zn mine wastes based geopolymers : Microstructure, technological and heavy metals adsorption properties

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This research investigates the effect of Pb-Zn mine wastes from Tunisian abandoned districts as filler on the mechanical performance and heavy metal's adsorption capacity of the metakaolin-based geopolymers. The mine waste was chosen as an inexpensive additive with high adsorption capacity, replacing metakaolin (0, 25, 50 and 75%) in the synthesis of four different geopolymers (MK100, MK75, MK50 and MK25, respectively). To produce geopolymers with low environmental impact, during the geopolymerization processes the SiO_2/Al_2O_3 and Na_2O/Al_2O_3 molar ratios were kept constant at 1, to reduce sodium silicate and sodium hydroxide to a minimum. The final products were studied by powder X-ray diffraction, 27Al and 29Si solid-state NMR and Scanning electron microscopy. Moreover, strength parameters and heavy metals Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+} adsorption tests were performed. The results show that geopolymerization in the presence of mine waste leads to an increase of the compressive strength of all blended geopolymers affording the highest strength (35.99 MPa at 28 days). The trend of heavy metals adsorption was found to be $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Cr^{3+}$. The maximum adsorption capacity of Cr^{3+} was highest for geopolymer with 100% of metakaolin (MK100).

Photocatalytic removal of toxic metal ions from water using functionalized g-C_3N_4

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Environmental pollution is increasingly becoming a global concern, as toxic materials from the ever expanding industrial sector continue to find their way into the surface and ground water resources. Significant parts of this industrial effluents are toxic metals, which are found not only to endanger human's health but are also harmful to aquatic lives [1].

Arsenic, cadmium, chromium, lead, and mercury are ranked among the priority metals that are of great concern to public health because of their high degree of toxicity [2]. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) [3, 4]. These elements exist in ionic forms in solution, and the following oxidation states: As(V), Cd(II), Cr(VI), Pb(II) and Hg(II) have been reported to be very toxic among the metal ions present in the environment [3, 5]. Hence, their removal is necessary in order to achieve a green environment. Heterogeneous photocatalysis is preferred for the removal of these toxic metals because it offers the advantage of either destroying the pollutants or converting them to a non-toxic and useful form, in contrast to conventional techniques (such as adsorption and ion exchange) that only transfer the contaminants from one phase to another thereby creating secondary pollution. In addition, photocatalysis relies on cheaply available light energy and semiconductor photocatalysts. Graphitic carbon nitride (g-C_3N_4), a polymeric semiconductor, has recently attracted attention as photocatalyst. It possesses many advantages such as excellent chemical stability, tunable electronic structure, and medium band gap (2.7eV) [6]. Therefore, the focus of this research is to remediate these toxic metal ions from water using heterojunction systems synthesized from graphitic-C_3N_4 incorporated with ternary nanoparticles as photocatalysts. The large surface area, ease of functionalization, economic feasibility and environmental friendliness of g-C_3N_4 makes it an ideal material for the preparation of nanocomposites for adsorption of toxic metals and the subsequent photocatalytic reduction of these metals to their non-toxic forms.

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Anion Exchanger on the base Polyvinylchloride for Efficient Removal Hexavalent Chromium Ions in Aqueous Media

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Present work, we studied the process of obtaining anion exchanger by chemical modification of plasticized polyvinylchloride with polyetilenpolyamine (PEPA). To study the structure morphology of the PPE-1 anion exchanger different characterization techniques such as XRD, FTIR, and SEM were applied. Moreover, the synthesized anion exchanger PPE-1 was used as effective removal for hexavalent chromium ions in aqueous media. Among the toxic metal ions, chromium is one of the widely used elements in industrial processes, such as metal finishing, textile dyeing, coating, pigments, batteries, leather tanning, etc. [1, 2]. Therefore, the wastewater of such an enterprise contains huge amounts of chromium ions. That why The World Health Organization (WHO) has recommended that the maximum permissible concentration of total chromium in drinking water be less than 0.05 mg/L [2]. Corresponding adsorption kinetics best fit the pseudo-second order model that followed a Freundlich isotherm. In the case of hexavalent chromium ions, the maximum adsorption capacity of PPE-1 was 218,4 mg/g. Thermodynamic data revealed spontaneous endothermic processes and was a chemisorption reaction. In addition, results show that the anion exchanger (PPE-1) has 98% for removing hexavalent chromium ions containing from wastewater.

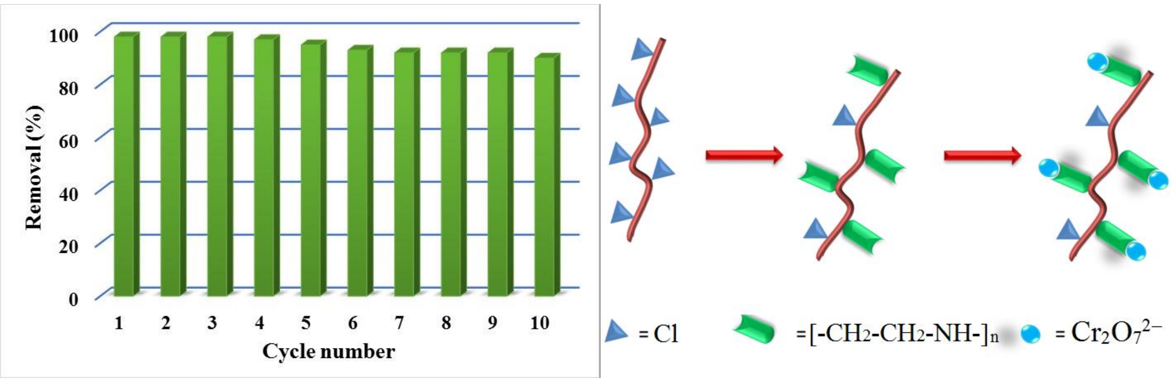

Figure 1. Sorption cycles of Cr (VI) ions by anion exchanger.

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DEVELOPMENT OF NEW HOMOGENOUS CATALYSTS FOR CO_2 REDUCTION TO FORMATES.

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The huge consumption of fossil resources and the resulting CO_2 emission has motivated scientists to develop benign and unlimited energy systems based on renewable resources.[1] The increase in energy demand has led to cleaner generation of energy from hydropower, wind and photovoltaic energy. Researchers are now focused on the utilization of carbon dioxide and biomass as a carbon resource for the chemical industry as opposed to the use of fossil reserves.[2] The disadvantage of relying on fossil fuel include: i) depletion of fossil reserves; ii) the negative impact of the current energy production on the environment, specifically the emission of greenhouse gases along with global warming.[3] The hydrogenation of carbon dioxide is a promising process because carbon dioxide is abundant, inexpensive and is C_1 source which is non-toxic, non-flammable and non-corrosive. The utilization of CO_2 requires high energy hence catalysts are required to overcome kinetic and thermodynamic stability.[4, 5, 7] The heterogenous hydrogenation of CO_2 is usually carried out under harsh conditions (high temperatures and pressure) and shows low selectivity and unsatisfactory activity, resulting in extensive energy consumption therefore homogenous hydrogenation is of interest.[6] High catalytic activity for homogenous hydrogenation of carbon dioxide has been widely investigated using complexes of iridium and ruthenium.[7-8] Herein, we investigate the application of new palladium pincer complexes in the hydrogenation of carbon dioxide to formate (Figure 1).

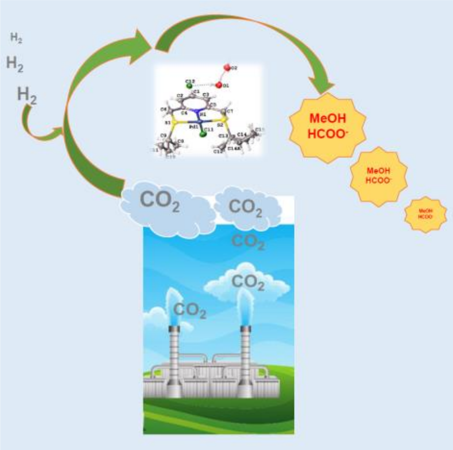

Figure 1: Illustration of CO_2 hydrogenation to formate.

Keywords: hydrogenation, carbon dioxide, palladium, pincers, formats
Acknowledgements: University of Johannesburg, Sasol and NRF

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ASSESSMENT OF THE QUALITY OF WATER IN DAMS AND LAKES: A STUDY OF OYUN DAM AND AFELELE LAKE IN OYUN AND OFFA LOCAL GOVERNMENT AREAS OF KWARA STATE

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This study investigated the quality of water in Oyun dam and Afelele Lake in Oyun and Offa Local Government Areas of Kwara State, Nigeria. To achieve this purpose, physicochemical quality parameters and selected trace metals determination were assessed. Specifically, the Nigeria standard for drinking water quality (NSDWQ) and world health organization (WHO) 2011 standard were adopted. Five water samples were randomly selected at different points of Oyun dam and Afelele lake for a period of five (5) months; i.e. from January to May 2018. The physical parameters were determined using the standard methods while the trace metals were determined via Atomic Absorption Spectroscopy (AAS). The results obtained showed that, the level of trace metals were Fe>Zn>Mn respectively in both locations; i.e. Oyun dam and Afelele lake. Cr was not detected due to the fact that, no mechanical activities within their surroundings. The nitrate levels of concentration in all the water samples were found to be below the World Health Organisation's (2011) standard and NSDWQ's standards. Based on the results obtained, the study concluded that the quality of the water in the dam and lake is not suitable for human consumption without adequate treatment. The result obtained was to due to unhealthy waste dispos

Preparation of high surface area zeolite templated carbons using coal fly ash-derived zeolite X for carbon dioxide capture applications

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The main focus of this study was to prepare zeolite templated carbons (ZTCs) as CO_2 adsorbents. ZTCs are often formed by depositing a carbon precursor into the zeolite channels, followed by carbonisation and ultimately acid etching of the inorganic zeolitic component. The templating method can be based on either a one-step or two-step process. In this study, coal fly ash derived-zeolite X was employed as the sacrificial template.[1] For the one-step process, ethylene carbon precursor was deposited at 700 °C and thereafter carbonised at 900 °C. During the 2-step process, furfuryl alcohol was initially impregnated into the zeolite pores and subsequently polymerised at 80 °C and 150 °C. After that, ethylene was deposited at 700 °C and then followed by carbonisation at 900 °C. All the resulting samples were etched with acids to derive a purely carbonaceous material. The properties of the resulting ZTCs were investigated using scanning electron microscope (SEM), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) analysis. As expected, the resulting templated carbon material portrayed similar morphological characteristics as the parent zeolite. The XRD results exhibited structural regularity mimicking that of parent zeolite by exhibiting a peak at $2\theta = 6 - 7$ °. The surface area and porosity analyses of ZTCs showed enhancements compared to the parent zeolite sample, which led to higher CO_2 adsorption.

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Synthesis and characterization of amine functionalized cellulose-silica composites for heavy metal adsorption in contaminated water.

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Heavy metal ion contamination in fresh water supplies (cadmium(Cd(II)), chromium(Cr(VI)), and lead(Pb(II)) has posed a major safety threat to drinking water worldwide. However, because of the impact on human health, controlling water contamination and wastewater treatment is a challenging task around the world. This research work is therefore, focused on fabricating a novel adsorbent derived from renewable resource, cellulose, extracted from banana stem fibres reinforced with silica nanoparticles functionalized with amino silane via *in situ* sol-gel method for heavy metal adsorption in contaminated water. So far, FTIR analysis confirmed successful extraction of cellulose fibres when compared to commercial cellulose. The results revealed that all spectra had broad peaks of OH stretching, which is due to moisture absorption. The stretching vibration of O–H groups is linked to broader absorption band observed in 3332 cm^{-1} in Figure 1*(a), (b)*. The C–H stretching vibration of the (Methylene) groups of cellulose is linked with the peak at 2896 cm^{-1}. The FTIR absorption bands at 1425 cm^{-1} and 1371 cm^{-1} relate to cellulose bending vibration C-H (Methylene) and C-H (Methyl). The adsorbed water is characterized by the band at 1625 cm^{-1}, while the C–O–C groups of cellulose are represented by the sharp tiny peak at 1159 cm^{-1}. The broad sharp peak absorbed at the 1028 cm^{-1} region, as shown in Figure 1*(a), (b)*, is linked to the cellulose's C–O stretching vibration, which increases peak intensity after hemicellulose and lignin are removed. The C–OH bending is represented by the small peaks at respectively 667 cm^{-1} and 558 cm^{-1}.

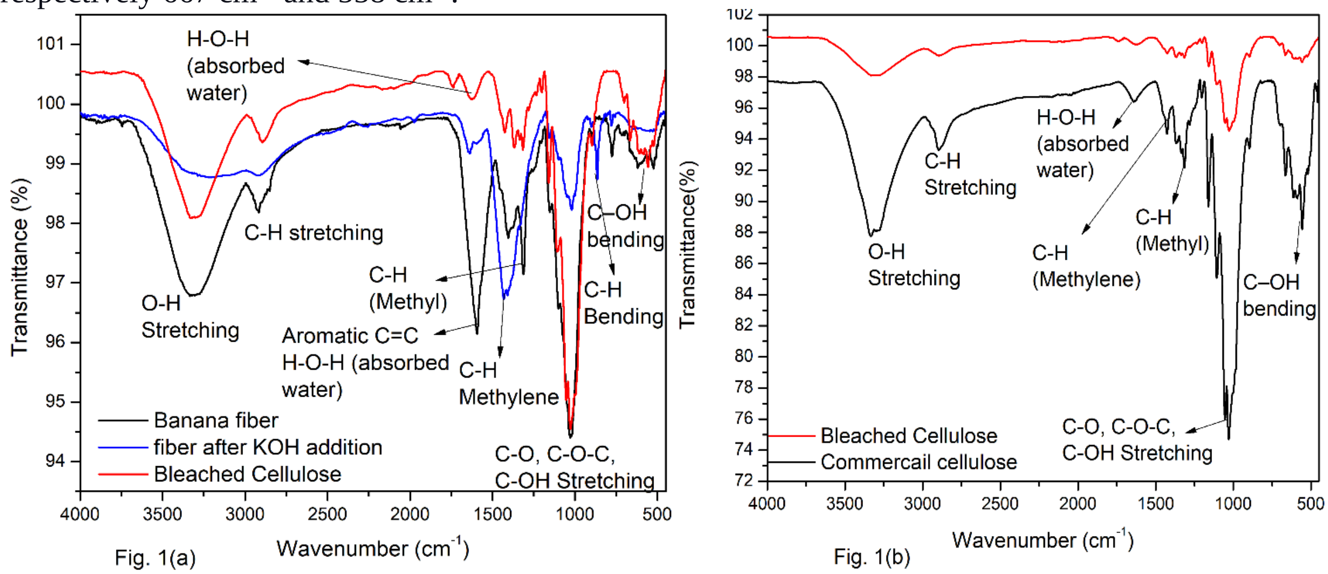

Fig. 1(a) Fig. 1(b)

Figure 1. *(a)* FTIR spectra of cellulose extraction step-by-step, *(b)* FTIR spectra of bleached and commercial cellulose

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ASSESSING THE BIOCHAR EFFECTS ON NUTRIENTS OF NYABUGOGO WETLAND IRRIGATION WATER

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Most people used wetland water for irrigating the vegetables, legumes and crops. The amount of nutrients varies depending on region and other factors. Nyabugogo wetland irrigation water also possesses those nutrients but amount is unbalanced and sometimes insufficient for plants growth. The amount of nutrients was measured for nitrate, nitrite, ammonium and phosphate and the amount was still below the standard values of irrigation water set by Rwanda Standards. *Eucalyptus Ceasia* biochar produced at temperature between 300 °C and 600 °C which is commercially available, was used as an alternative way of providing the nutrients by increasing phosphate and varying nitrogen form concentrations of the irrigating water of Nyabugogo wetland and tested the effect of *Eucalyptus Ceasia* biochar has on pH, TDS and conductivity. The experiment was performed by using column glasses at room temperature and involved measuring level of nitrate, nitrite, ammonium, phosphate, conductivity, TDS and pH of irrigating water before and after running column chromatography. By using UV VIS Spectrophotometer, the results showed that nitrate and nitrite amount decreased with increase in ammonium concentration. Phosphate amount was suddenly increased. pH, conductivity and TDS were also increased as time moved.

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Detection of Methylene Blue from textile by Differential Pulse Voltammetry Using Cobalt Hexacyanoferrate Modified Carbon Paste Electrode

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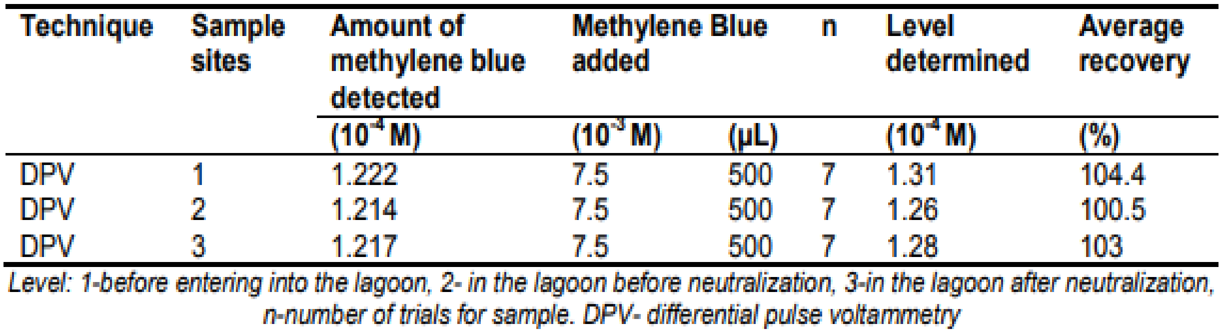
Modified carbon paste electrode (CPE) by cobalt hexacyanoferrate (CoHCF) was prepared and the sensitivity of the prepared electrode was analyzed by differential pulse voltammetry. The electrochemical behavior of methylene blue on cobalt hexacyanoferrate modified carbon paste electrode (CoHCF / MCPE) has been investigated by differential pulse voltammetric technique. Also the detection limit of modified electrode was investigated on methylene blue dyes from textile industrial waste water. By the prepared electrode 1.222×10^{-4} M, 1.214×10^{-4} M and 1.217×10^{-4} M Methylene blue was detected in the textile effluent at three sample sites and 100.5 to 104.5 % of recovery was calculated. The prepared and modified electrode was efficiently detects 1.053 x10-6 limit of detection.

Table1: Assay results of methylene blue in spiked textile waste water samples adopting the differential pulse voltammetry technique



Technique	Sample sites	Amount of methylene blue detected	Methylene Blue added		n	Level determined	Average recovery
		(10^{-4} M)	(10^{-3} M)	(µL)		(10^{-4} M)	(%)
DPV	1	1.222	7.5	500	7	1.31	104.4
DPV	2	1.214	7.5	500	7	1.26	100.5
DPV	3	1.217	7.5	500	7	1.28	103

Level: 1-before entering into the lagoon, 2- in the lagoon before neutralization, 3-in the lagoon after neutralization, n-number of trials for sample. DPV- differential pulse voltammetry

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Synthesis and Characterization of Co-doped Nickel-ZnO/Polypyrrole Nano-composites, and their Effect on Photo-catalytic Degradation of P-nitrophenol under Solar Irradiation

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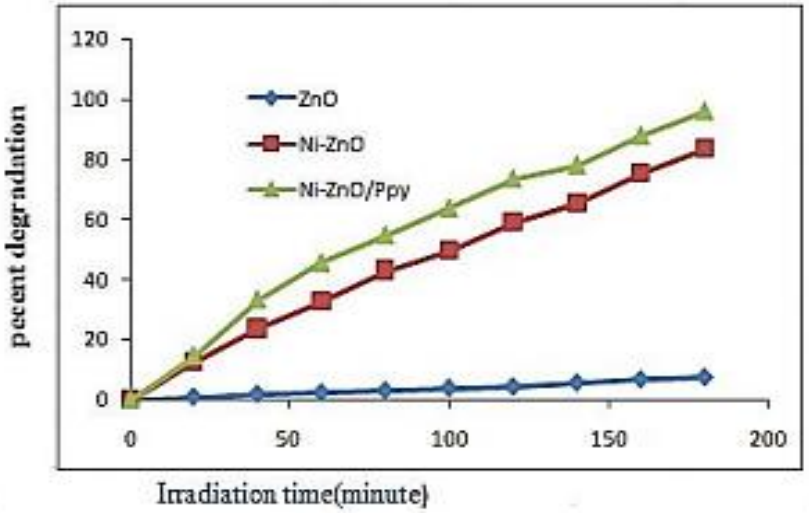
Nickel-polypyrrole co-modified ZnO nano-composites (Ni-ZnO/Ppy) were synthesized by two methods, metal impregnation of nickel (Ni) and In-situ chemical polymerization of polypyrrole (Ppy) on ZnO nano-particles. The crystal size, band gap energy and bond structure of as-synthesized nano-composites were investigated by using x-ray diffraction(XRD),UV-Vis and Fourier transform infrared (FT-IR) spectroscopic techniques respectively. Photo-catalytic degradation efficiency of synthesized photo-catalysts was investigated on p-nitrophenol dyes under solar irradiations and Codoped photo-catalysts shows better catalytic degradation efficiency than both ZnO and Ni-ZnO nano-particles. Ni-ZnO/Ppy photo-catalysts effectively degraded 96.04% of p-nitrophenol dye on 180 minute visible light irradiation. Highest photo-catalytic activity of Ni-ZnO/Ppy nano-composites over ZnO photo-catalysts was attributed due dopants to the lower rate of recombination of the photo generated electrons- holes as well as its lower crystal size and band gap energy. The photocatalytic degradation of p-nitrophenol kinetically follows pseudo first-order reactions for Ni-ZnO/Ppy photo-catalysts



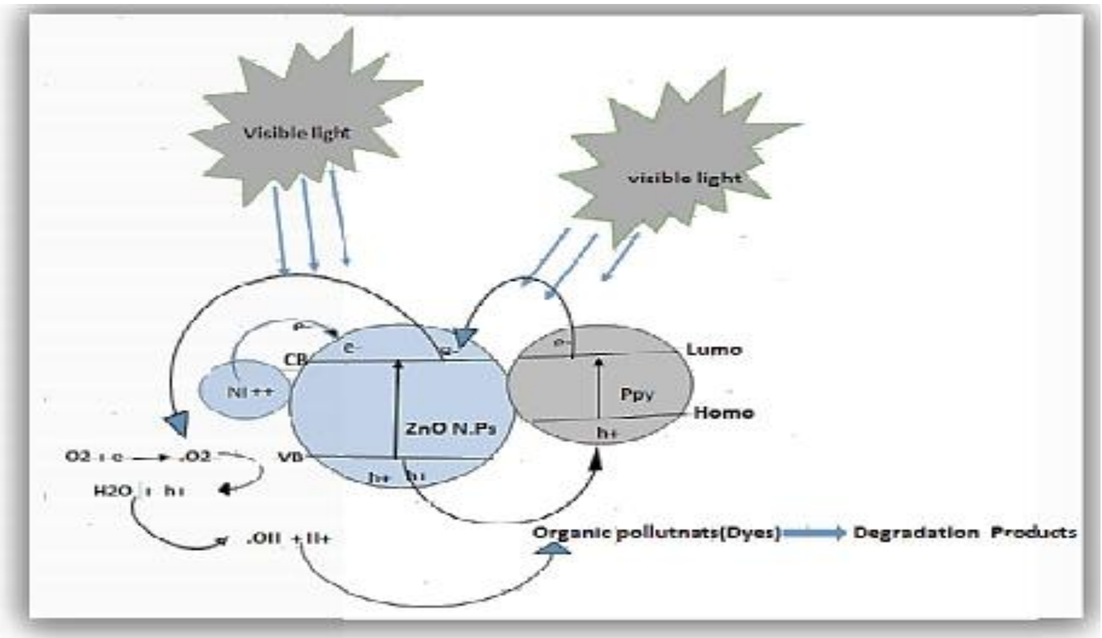


Figure1. Degradation mechanism and efficiency of degradation of catalysts under visible irradiations

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Emerging Environmental Pollutants: Neonicotinoid Insecticides and their Toxicity Towards Non-Target Organisms

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The neonicotinoid insecticides are an emerging class of environmental pollutants. They have been used and have been present in the environment all over the world for the last 30 years. Lately, these compounds have been under the spotlight and increasingly more research has been conducted on their toxicity, not only towards wildlife, especially pollinators, but also towards humans. The overall purpose of this review is to highlight the research results about their toxicity towards non-target organisms.

Neonicotinoids gained exceptional popularity all over the world since their release on the global market thanks to some outstanding characteristics of their: extremely high efficiency towards target organisms, affordability, and safety compared to other synthetic insecticides on the market.

Unfortunately, most of the studies done on these insecticides published in the last two years highlight actual toxicity of these active compounds to a great number of living species, not only to pollinators, fundamental for agricultural purposes, but also to humans. Consequently, controversies are arising around neonicotinoids and their metabolites as it seems that their potential toxicity and persistency in the environment have been initially underestimated.

To hinder neonicotinoids as environmental pollutants and toxic active substances, many countries and unions started to take action through bans, restrictions and limitations of these pesticides.

Overall, neonicotinoids should be better assessed and given more space and attention in public discussions.

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Sensors for monitoring the quality of the living environment

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We mistakenly think about pollution as something that only outside the home or indoors. On the contrary, even the air we breathe in our homes can be unhealthy. This is called "indoor pollution", closely related to the concept of Indoor Air Quality (IAQ). The consequences related to poor domestic air quality are connected a higher incidence of pneumonia, acute chronic respiratory infections, heart attacks, cardiovascular diseases and respiratory allergic diseases, found especially among the most sensitive population such as the elderly.

Pollutants that worsen air quality are coming from painted walls, from furniture and from detergents used for cleaning the house, and so on. Among the indoor chemical pollutants, formaldehyde is one of the most toxic volatile organic compound (VOC). The international agency for cancer research (IARC) classifies formaldehyde as a carcinogen. In our homes formaldehyde is present in low concentrations, however we must be careful because mainly accumulates in conditions of low temperature and low humidity. It is then released over time. It is present as bactericide and as a solvent for cosmetics and deodorants or is present in pressed wood products, plywood, fiber panels, glues and insulating coatings. In food industry, formaldehyde is used as food additive during the preparation, storage and marketing of products. In particular it is a preservative (under the heading E240) of smoked products and shellfish.
Exposure to formaldehyde at concentration levels in the 0,5-2 ppm range, symptoms of ocular irritation appear. As concentrations increase, there is irritation of the upper airways and, beyond 5 ppm of the lower airways. Finally, pneumonia, pulmonary edema and death occur for concentrations above 50 ppm. The WHO Guideline for Indoor Air Quality for formaldehyde (WHO, 2010) sets an exposure limit to 81 ppb (30-minute average concentration). The WHO guideline value is considered protective against both acute and chronic sensory irritation in the airways in the general population and in potential sensitive subpopulations including children and the elderly.

Our research group at the University of Messina, is actively involved in a project (4FRAILTY) for developing an intelligent indoor formaldehyde sensor. The objective of this research project is to develop a conductometric device based on metal oxides of reduced dimensions which is not only sensitive and selective, but which is able to process and communicate the acquired data. The technological innovation of the sensor will be also its miniaturization and networking capacity. The sensor developed will be then simple and reproducible by the industries of the microelectronics sector, useful for the monitoring of indoors in order to protect people's health and in particular to protect the most fragile people such as the elderly and children who spend more time at home.

We thanks the 4FRAILTY (Intelligent sensoring, infrastructure and management models for the safety of fragile entities) for the financial support.

Estimating net oxygen released by the restored mangrove forests

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Mangrove release oxygen during photosynthesis. They utilize energy from sunlight to make organic carbon by using carbon dioxide and water. In this process 6 molecules of carbon dioxide are used and 6 molecules of oxygen get released as by-product. To achieve positive net oxygen production, mangrove need to store the fixed organic carbon in their body biomass and underlying soil, reduce the decomposition rates or increase the rate of oxygen production as seen in rapid growing mangrove seedlings. While mangrove restoration efforts have been carried out to aid in carbon sequestration, less attention has been given to the role that these artificial forest play in oxygen production.

We estimated the amount of oxygen released by the restored mangrove forests using the previously reported carbon sequestration rates [1, 2 & 3]. Net oxygen released was determined according to [4]. Results show that the net oxygen release by the restored mangrove forests aged between 8 – 10 years were 4 ± 1.1, 27.1 ± 0.0 and 25.4 ± 0.0 tonnes ha^{-1} y^{-1} at Bali Indonesia, Khanom in Thailand and at a site in Malaysia respectively. These values may be even higher than those reported from their natural counterpart mangrove strands, global average, and the one measured from a reference pristine mangrove site in Florida (Table 1).

Table 1: Net O2 release (in tonnes ha-1 y-1) by the restored mangrove forests in Southeast Asia

Location	Author	C sequestration (tonnes ha-1 y^{-1})	Net O_2 Release (tonnes ha-1 y^{-1})
Restored sites			
Bali, Indonesia	Sidik[1]	1.5 ± 0.4	4.0 ± 1.1
Khanom, Thailand	Matsui[2]	8.3± 0.0	22.2 ± 0.0
Malaysia	Sanderman [3]	9.5 ± 0.0	25.4 ± 0.0
Natural sites			
Bali, Indonesia	Sidik[1]	2.2 ± 0.6	5.9 ± 1.6
Sawi Bay, Thailand	Alongi[5]	1.84 – 2.81	4.9 – 7.5
Matang reserve, Malaysia	Alongi[6]	1.48 – 4.1	3.9 - 10.9
Global overall average	Alongi[7]	1.74 ± 00	4.64 ± 00
Reference pristine site at Florida	Marchio[8]	1.62 ± 05	4.32 ± 13

Keywords; Restored mangroves, Net oxygen production, Carbon sequestration, Molecules

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Feasibility study on the monitoring and quantification of Nitrogen, Phosphorus and Potassium on hydroponic cultures

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In hydroponic cultivation, monitoring and quantification of nutrients is of paramount importance. Accurate, robust sensors for detection of Nitrogen, Phosphorus and Potassium (NPK) would be desired in horticultural production. Spectroscopy can be used for this, but other nutrients interfere and hinder accurate and reliable quantification.

In order to better understand and solve nutrients' interferences, an orthogonal experimental design has been used, based on Hoagland fertilizer solutions, a widely used complete and complex nutrient mixture. The experimental factorial design consisted of eight orthogonal levels of N, P and K rendered on 83 of different samples of Hoagland solution, each one with its own specific concentration of NPK. Concentration ranges were varied in a target analyte independent style: [N]= [103.17-554.85] ppm; [P]= [15.06-515.35] ppm; [K]= [113.78-516.45] ppm, by dilution from individual stock solutions. This strategy allowed the variation of each parameter individually, maintaining the remaining constant, enabling the individual variations as well as their correlations to be obtained. A UV-Vis-based Artificial Intelligence-enhanced (AI) system was used for quantification of NPK on the analysed samples. It featured an advanced processing algorithm named Self-Learning Artificial Intelligence (SL-AI).

From the analysis of the acquired and processed data, it was possible to understand that N spectral features are dominant, whereas P and K will behave as interferents, with information on P properties not being very evident on spectra. The obtained results allowed very good quantifications for N and K, with errors of 6.7% (0.997) and 3.8% (0.987), respectively, to be achieved. Regarding P, as expected, only satisfactory results were obtained, corresponding to a qualitative grade. The developed system can be of great potential for monitoring and quantification of NPK in hydroponic platforms.

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Investigation of Pyrolysis Aqueous-Phase Fraction as a Possible Feedstock for Mixed Microbial Cultures

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Nowadays, climate change and the consumption of a growing amount of energy and material are highlighting, each day more, the necessity to adapt new strategy for the developing of green solutions. Biorefineries can be considered as a possible solution, both for energy and material production, that can provide the needs without impact climate and ecosystems. In particular, biomasses are a wide possible source of material and energy which utilization could allow, at the same time, the reduction of greenhouse gasses (GHG). However, due to the large variability of the possible source, a biorefineries able to treat biomass and obtain few valuable chemicals/materials it's not been yet developed. A possible road to follow it's the thermochemical-biological conversion of wooden biomass, with an initial thermal degradation, such as pyrolysis, followed by a biological conversion with Microbial Mixed Cultures (MMC). Pyrolysis is the thermal degradation that occur in absence of oxygen and it's able to break down the macromolecules that form wooden biomass, yielding a solid (biochar), a liquid (bio-oil), and incondensable gases (syngas) [1]. Biooil can be easily divided into a yellowish water-soluble fraction (Aqueous Phase Liquid, or APL) and a dark red-brown water-insoluble fraction (Pyrolytic lignin). APL is composed of a variety of different molecules, however MMC are known to be able to deal with heterogeneous substrates and convert them into few valuable products such as Volatile Fatty Acids (VFAs) or Alcohols (ROH), which can be used as platform chemicals for the production of materials, fuels and chemical solvents. In particular, APL can have different amounts of anhydro-sugars (e.g. Levoglucosan) which are a suitable substrate for microorganisms [2]. However, bio-oil is rich also in several inhibiting substance, such as furans and phenols that may have inhibitory effect for the fermentation [3,4]. In this study, Chemical Oxygen Demand (COD) was used as energy tracker to determine the quantity of energy flowing into syngas and APL component, that can be used for further fermentation. In fact, COD it's directly correlated with the energy content, in particular 1 Kg of COD (or KgO) it's almost equal to 15 MJ of energy [5]. Also, considering the COD of oxygen as -1 KgO/Kg, it's possible to make balance between inputs and outputs in close systems. Pyrolysis of different biomasses were performed at different temperatures, in particular, a close pyrolysis system was developed to allow the gas recirculation through the pyrolyzer, with the aim to concentrate the syngas (Figure 4). Nitrogen was used to remove all the air from the system. After the pyrolysis APL was collected in a water trap (kept at 0°C), pyrolytic lignin and tars were trapped in a cotton filter, and Syngas was collected in a gasbag, which allow the system to maintain atmospheric pressure. Biochar was removed from the quartz tube reactor after the cool down of the system. Elemental analysis allowed the determination of COD's of pyrolytic lignin and biochar, GC-TCD was used for the determination of gas's COD, and APL's COD was directly determined with a LAR COD analyzer. Moreover, APL was further investigated with different derivatization techniques and analyzed with GC-MS, reveling the presence and variation of some key molecules.

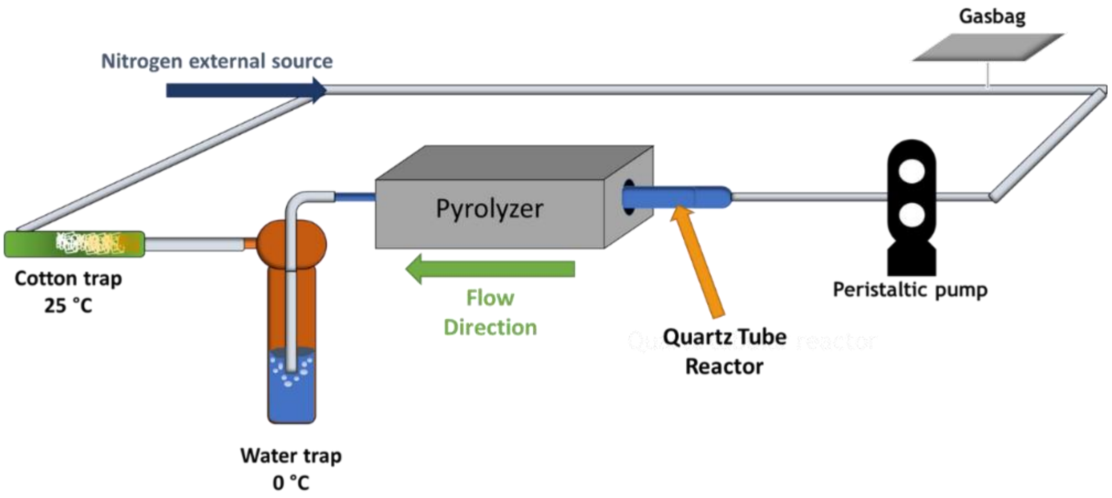

Figure 4. Scheme of pyrolysis set-up experiments

Initially, three different biomass types were investigated: Fir, Switchgrass, and Cellulose. The pyrolysis temperature was kept at 550°C for each biomass. Around 90% of COD recovery was performed for all the analysis, reviling higher yield of potentially fermentable compounds in fir sawdust and switchgrass respect pure cellulose (Figure 5).

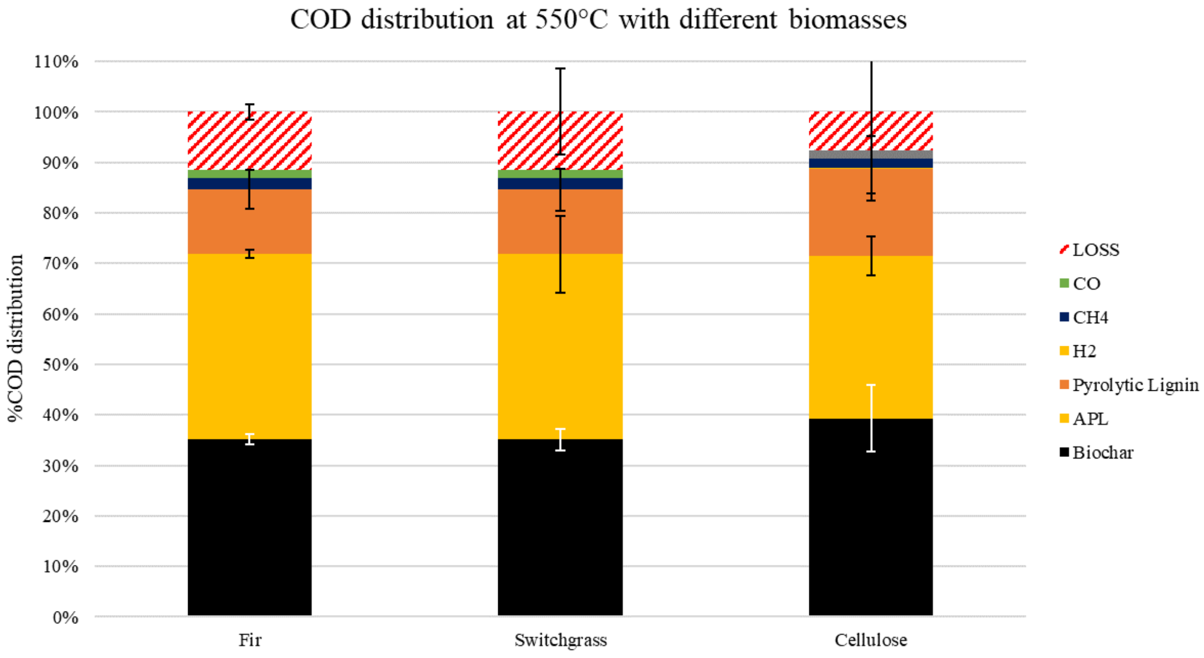

Figure 5. %COD yield in the recovered pyrolysis products

Chemical characterization performed on APL, showed however higher yield of anhydro sugars from cellulose. Fir had higher amount of phenols and furans, which may have inhibitory effect.

Further, Fir was selected to evaluate the variation of APL components and COD distribution with temperature. Several experiments were performed, from 400°C up to 700°C with a step increase of 50°C, reveling a gradually increase of APL %COD yield until 600°C, with a maximum of 44%COD yield. From 600°C to 700°C the yield of APL and WI result stable, with a gradually decrease of biochar and an increase of syngas yield (Figure 6).

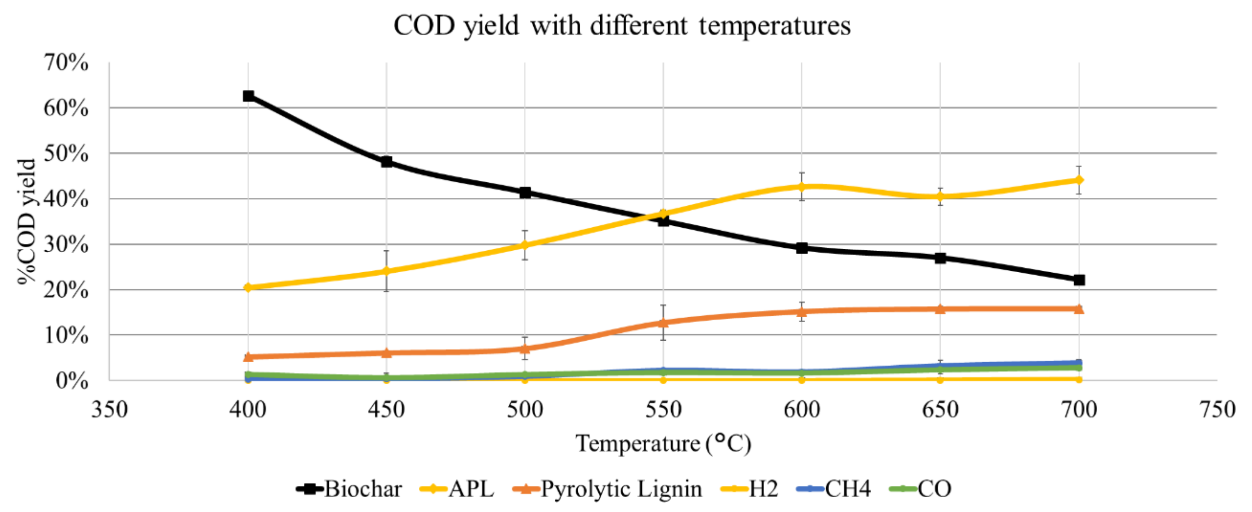

Figure 6. %COD yield of Pyrolysis Products within Temperature

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New urease inhibitors of agricultural interest from pyrolysis products

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Nitrogen is one of the essential elements for the optimal growth and development of crops. For this reason, large quantities of nitrogen fertilizers are used on agricultural fields every year [1]. Urea is one of the most used N fertilizer worldwide, however, the massive use of urea involves several environmental issues. The urease enzyme, naturally present in soils, rapidly hydrolyzes urea leading to the formation of gaseous pollutants (CO2 and NH3) and a general increase in soil pH, a process that negatively impacts plant growth [2,3]. The hydrolytic decomposition of urea by the urease enzyme has both environmental and financial impacts, as the efficiency of urea fertilizers is reduced due to the fast volatilization process of ammonia, which can lead to a loss of up to 40% of urea nitrogen [4].

In this study, some of the products obtained from the fast pyrolysis (550°, 5 minutes) of three lignocellulosic biomasses were evaluated as new urease enzyme inhibitors: Larch (Softwood), Poplar (Hardwood) and Panicum (Herbaceous). In particular, of the bio-oil produced by pyrolysis, the total water-soluble phase (WS_tot) was analyzed, as well as the two fractions obtained from its liquid-liquid separation with ethyl acetate (WS_EtAc) and water (WS_H2O). Pyrolysis made it possible to break down the lignocellulose into low molecular weight organic compounds with a catechol-like structure and into pure catechol molecules, one of the compounds known to be most effective in inhibiting the urease enzyme [5,6]. For this reason, the three products analyzed in this study have been evaluated by taking as a reference their content in catechol: in the assessment of urease inhibition capacity and the eco-toxicity tests, quantities of the product were used to provide 5ug of catechol per gram of soil used in the assay. The inhibitory capacity of the urease enzyme was evaluated by quantifying the ammonia produced in the soil by urea hydrolysis processes in the presence of the three tested inhibitors. Samples were incubated for 24 hours at 37°C, then the ammonia produced was distilled and quantified by titration. All three products tested showed promising enzyme inhibitory abilities: rates of inhibition over 50% were obtained from WS_tot and WS_EtAc. In general, the lignocellulosic biomass of origin does not seem to affect the inhibitory capacity of the products. Considering as the ultimate goal of the investigated products their application in the agricultural field, their phytotoxicity and toxicity on earthworms was also evaluated. Among the different products, WS_EtAc showed the lowest toxicity on cress seedling, and no negative effect on early growth of oat. Tests on earthworms showed non-toxicity of the products on invertebrate target organisms, except for WS_H2O obtained from pyrolysis of panicum, which caused severe mortality.

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Recovery of furanic compounds from steam explosion condensate in a full-scale forestry based biorefinery

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During steam explosion (STEX) of woody biomass a certain proportion of the hemicellulose sugars are converted into furfural and other furanic compounds. Such compounds are valuable, renewable chemical feedstocks for use in solvents, polymers and biofuels, and their recovery would be a significant economic contribution to the biorefinery. On the other hand, if not recovered, extensive cleaning of the aqueous effluent is required before release into the environment. Thus, the use of this byproduct as a resource is strongly indicated.

At the ArbaOne biorefinery in Norway, the steam from the full-scale STEX pretreatment of wood chips is condensed and the dissolved furfural and other organic constituents are recovered by stripping. In addition, further recovery of non-volatile products like HMF (hydroxy-methyl-furfural) by washing of the exploded material is under development. The production and recovery of the furanic compounds are regularly monitored by in-depth analysis of the condensates and filtrates. It is observed that the severity of the steam explosion conditions significantly influences the yields. The type of feedstock is also a determining parameter.

This paper presents examples of production and recovery of furanics at different STEX conditions based on full-scale production at the ArbaOne production plant. The underlying chemistry and the optimization of STEX severity is also discussed.

Biomass derived heterogeneous catalysts for the conversion of CO_2 into cyclic carbonates

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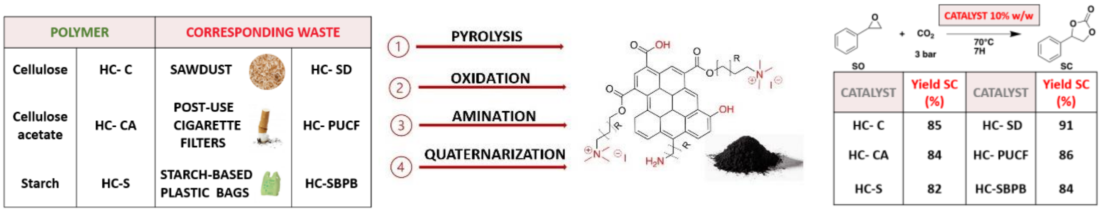
The synthesis of cyclic carbonates starting from epoxides is an interesting way to reuse CO_2, the major greenhouse gas present in the atmosphere. These products are mainly used indeed as alternative aprotic polar solvents in lithium batteries and as a starting material in polymer synthesis.[1] In our previous study we used bio-based eutectic mixtures based on choline salts ((2-hydroxyethyl) trimethylammonium halides) and various H-bond donors (HBDs), as bi-component catalysts to catalyze the synthesis of cyclic carbonates from epoxides and CO_2 under mild conditions (80 °C, 1-4 bar, 5-22 hours).[2]

The aim of the present work was to synthesize a heterogeneous version of the same catalyst, thus introducing these functional groups that were capable to catalyze the carbonatation of epoxide under homogeneous conditions. By applying pyrolysis to different pure biomass and wastes,[3] we prepared six chars that were then derivatized with both ammonium and HDBs moieties on their surfaces in a four-steps synthesis (Figure 1): i) pyrolysis, ii) oxidation, iii) introduction of an aminosilane group, iv) quaternarization of the amino group. With this synthetic pathway we prepared six catalysts from three different polysaccharides (cellulose, cellulose acetate and starch) and three types of waste mainly made from the same polysaccharides (sawdust, post-use cigarette filters and starch-based plastic bags).

The analysis (Raman, ATR-FTIR and XPS) made on these catalysts and their precursors demonstrate that: (i) each reaction step was successfully performed; (ii) there are no clear differences in the functional groups present on the surface of the different materials; (iii) both iodide and various types of H-bond donor functionalities are present (i.e., $-NH_2$, -COOH, Si-OH), thus demonstrating the bi-functionality of the catalysts. The catalysts had very good activity on the synthesis of cyclic carbonates from epoxides in mild conditions; moreover, they were fully recyclable. The results showed a similar behavior for all the six catalysts, demonstrating the versatility of the synthetic pathway (Figure 1) on different types of pyrolysis products.



POLYMER		CORRESPONDING WASTE	
Cellulose	HC- C	SAWDUST	HC- SD
Cellulose acetate	HC- CA	POST-USE CIGARETTE FILTERS	HC- PUCF
Starch	HC-S	STARCH-BASED PLASTIC BAGS	HC-SBPB

CATALYST	Yield SC (%)	CATALYST	Yield SC (%)
HC- C	85	HC- SD	91
HC- CA	84	HC- PUCF	86
HC-S	82	HC-SBPB	84

Figure 1. Synthesis of the catalysts and their application on CO_2 conversion

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Design of bifunctional catalysts from mesostructured acidic oxides for CO_2 conversion to dimethyl ether

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CO_2 is widely recognised as the main cause of greenhouse effect, causing global warming and climate change. With the aim to reduce CO_2 emissions, several strategies have been developed for the capture, utilization, and storage of CO_2 (CCUS). This work focuses on the development of bifunctional catalysts for the conversion of CO_2 into dimethyl ether (DME), a fuel with no collateral emissions other than CO_2 and H_2O, a high cetane number and chemical-physical properties similar to LPG. DME is obtained from the reaction of CO_2 with H_2 through two subsequent reactions. The first one is the CO_2 reduction with H_2 to obtain methanol; this reaction is promoted by Cu-based catalysts like $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$. The second one is the dehydration of methanol to DME, catalysed by solid acidic catalysts, such as zeolites and γ-Al_2O_3 [1]. In this work three different types of mesostructured acidic catalysts were synthesized: Al-SiO_2 (Al-SBA-15, Al-MCM-41), Zr-TiO_2 and γ-Al_2O_3. These materials were tested for methanol dehydration and used as supports for the Cu-based redox phase, to obtain composite materials to be used as bifunctional catalysts. Mesostructured matrix should limit the growth of redox phase nanoparticles inside the pores, assure a high dispersion due to the high surface area, leading to a high contact area between the two phases granting, in theory, superior catalytic performances.

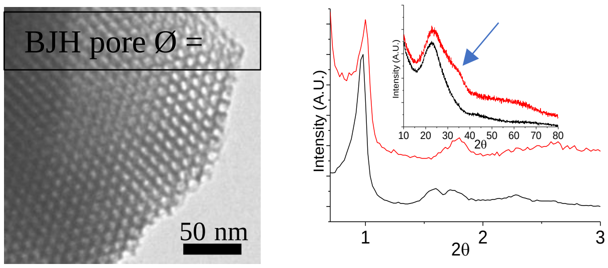

Figure 1. TEM and XRD of Al-SBA-15 (black) and composite (red)

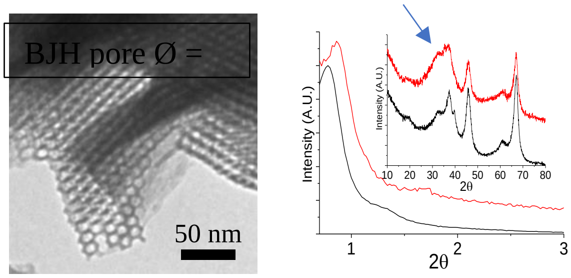

Figure 2. TEM and XRD of γ-Al_2O_3 (black) and composite (red)

All mesostructured systems were synthesized via the Sol-Gel method, either through an Evaporation-Induced Self-Assembly (EISA) or a solvothermal approach, and characterized by XRD, TEM and N_2 physisorption. Acidic sites characterization was performed by calorimetry and FTIR spectroscopy using pyridine as a probe molecule. The catalysts were mixed with a $Cu/ZnO/Al_2O_3$-based commercial redox catalyst and tested in a bench-scale plant for CO_2 conversion to DME. Mesostructured supports were used to disperse the $CuO/ZnO/ZrO_2$-based redox phase by a wet impregnation method combined with a self-combustion process. The obtained bifunctional catalysts were characterized by PXRD, N_2 physisorption, TEM and HRTEM to determine the most promising synthetic conditions in terms of dispersion and nanosize of the active phase and textural properties of the corresponding composites.

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Synthesis and characterization of functional sol-gel based geopolymer matrices used for the conservation and restoration of cultural heritage

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Geopolymers are inorganic materials composed mainly of aluminates and silicates, similar to ceramics [1]. Geopolymerization is a process that occurs by treating inorganic materials of orthosilicate and aluminate with an alkaline solution such as sodium or potassium hydroxide. Natural clays are commonly used in the synthesis of geopolymers, in particular, this work focuses on the chemical manipulation of the geopolymer, through the use of sol-gel hybrid coatings of alkoxysilane nature. The sol-gels used serve to improve the properties of geopolymers, such as mechanical and thermal resistance, water repellency, chemical inertness, and porosity of the material for potential applications in the restoration and conservation of cultural heritage [2]. The synthesis of functionalized geopolymers consists of the pre-treatment of the mixture of geopolymers with alkoxysilane sol-gels and a siloxane crosslinker [3]. The alkoxysilanes selected have aromatic hydrocarbon groups or linear or branched long-chain aliphatic hydrocarbons [4]. The corrosion resistance and hydrophobicity of these geopolymeric monoliths are tested by immersion and wettability tests; microbial growth tests were also conducted to verify the antibacterial and antifouling activity. Other physico-chemical characterizations were performed to verify the implemented surface properties concerning those of the untreated geopolymer precursors.

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Hierarchical Metal–Polymer Hybrids for Enhanced CO_2 Electroreduction

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The design of catalysts with high activity, selectivity, and stability is key to the electroreduction of CO_2. Herein, we report the synthesis of 3D hierarchical metal/polymer–carbon paper (M/polymer-CP) electrodes by in situ electrosynthesis. The 3D polymer layer on CP (polymer-CP) was first prepared by in situ electropolymerization, then a 3D metal layer was decorated on the polymer-CP to produce the M/polymer-CP electrode. Electrodes with different metals (e.g. Cu, Pd, Zn, Sn) and various polymers could be prepared by this method. The electrodes could efficiently reduce CO_2 to desired products, such as C_2H_4, CO, and HCOOH, depending on the metal used. For example, C_2H_4 could be formed with a Faradaic efficiency of 59.4 % and a current density of 30.2 mA cm^{-2} by using a very stable Cu/PANI-CP electrode in an H-type cell. Control experiments and theoretical calculations showed that the 3D hierarchical structure of the metals and in situ formation of the electrodes are critical for the excellent performance.

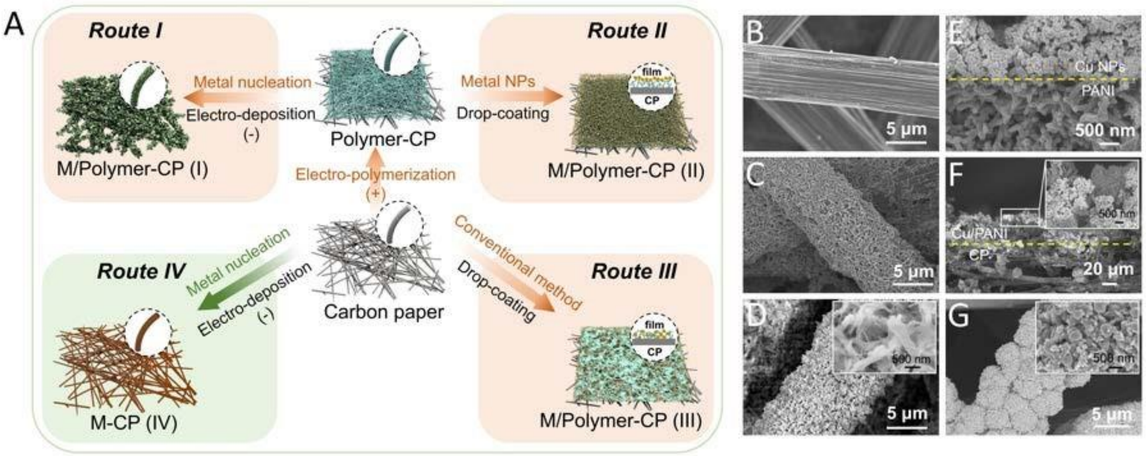

Figure 1. A) Process used to prepare various electrodes. B) SEM image of CP. C) SEM image of PANI-CP obtained after electropolymerization for 1 min. D) SEM image of Cu/PANI-CP (I) electrodes obtained after metal electrodeposition for 10 min (inset: high-magnification image). E) Cross-section image of the Cu/PANI-CP (II) electrode. F) Cross-section image of the Cu/PANI-CP (III) electrode (inset: high-magnification image). G) SEM image of the Cu-CP (IV) electrode (inset: highmagnification image).

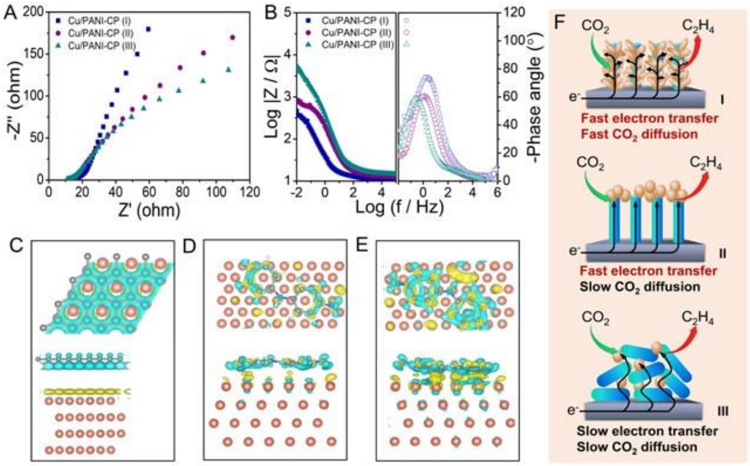

Figure 2. A) Nyquist and B) Bode plots of Cu/PANI-CP (I), Cu/PANI-CP (II), and Cu/PANI-CP (III) electrodes in CO_2 saturated 0.1 M KCl solution at equilibrium potential for CO_2 reduction; Charge difference density from top and side views of C) Cu-CP (for Cu-CP (IV)), D) Cu/PANI (for Cu/PANI-CP (II) and Cu/PANI-CP (III)), and E) $Cu_{(vacancy)}$ /PANI interfaces (for Cu/PANI-CP (I)). The atoms in orange, silvery, blue, and white represent Cu, C, N, and H, respectively. Yellow and blue regions correspond to electron excess and electron deficiency sections. The isosurface value was set to 0.0001, 0.002, and 0.002 *e* $Å^{-3}$, respectively; F) Scheme of the CO_2 diffusion and electron transfer on various Cu/PANI-CP electrodes with different structures.

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Synthesis of Higher Carboxylic Acids via the Hydrocarboxylation of Alcohols with CO_2 and H_2

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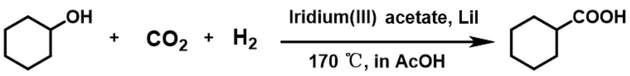
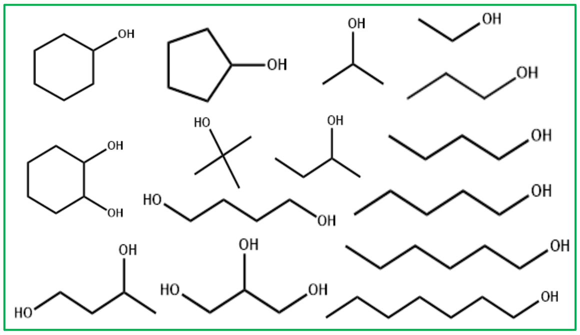
Carbon dioxide (CO_2) is an abundant, availability, recyclability and environment friendly one-carbon (C1) building block. The effective utilization of CO_2 is of great scientific and social significance to alleviate environmental problems and energy crisis. Carboxylic acid is a key intermediate in industry, especially in fine chemical industry. The straightforward route of preparing higher carboxylic acids from abundant CO_2 and renewable H_2 is a very attractive research field. Herein we provided a protocol of synthesizing higher carboxylic acids via alcohols with CO_2 and H_2 in acetic acid (Scheme 1). The catalytic system was efficient, high active and selective consisting of Iridium(III) acetate and LiI. The reaction can work at above 120 °C and the catalytic system had a wide substrate scope (Figure 1). The mechanism indicates the alcohols were first converted to olefins rapidly and then to alkyl iodides and/or acetates, followed by oxidation addition and reduction elimination reactions, the higher carboxylic acids were produced ultimately. CO was generated by RWGS reaction (Figure 2). To our knowledge, it is the first report of higher carboxylic acids synthesis by alcohols, CO_2 and H_2 using an iridium catalyst.



Scheme 1 Synthesis of higher carboxylic acids via alcohol, CO_2 and H_2.



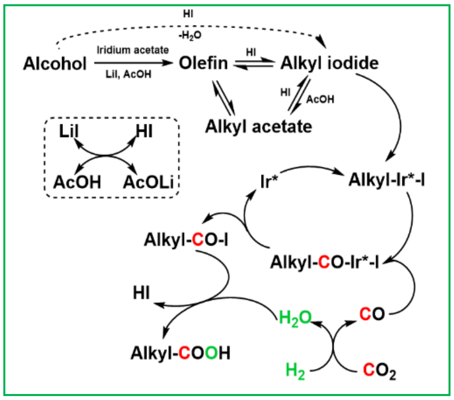


Figure 1 Various substrates.

Figure 2 The proposed reaction mechanism**.**

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DFT Assisted Predesign of Photocatalysts for Carbon Dioxide Reduction

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Light-driven carbon dioxide reduction offers an economical solution to global warming and fuel production. But nowadays, most photocatalysts for carbon dioxide suffer from various disadvantages, like high cost or require additional reductants. Herein, we developed serval kinds of photocatalysts for carbon dioxide reduction, which cost low and have relatively high performance. The best of our results reached over 100 μmol·g^{-1}·h^{-1} under visible light.

Table 1. Molecular orbit information of various structures.

NO.	Symmetry	Donor	Acceptor	Linkage	Basis Set	HOMO (eV)	LUMO (eV)	Band gap (eV)	Wave length (nm)	EP Red (V)	EP Ox (V)
A07	C3	TPA	Triazine	Azo	6-31g(d)	-5.2306	-2.6335	2.5971	477.40	-1.866	0.731
A07A	C3	TPA	Triazine	Azo	def2tzvp	-5.5264	-2.9747	2.5516	485.91	-1.525	1.026
084-01	S6	C10H8	Triazine	C-C	6-31g(d)	-5.8907	-2.2036	3.6871	336.26	-2.296	1.391
084-02	C3	TPA	Triazine	C-C	6-31g(d)	-5.1519	-1.7579	3.3941	365.30	-2.742	0.652
084-03	C6	TPA	AQ	C-C	6-31g(d)	-5.1498	-2.7236	2.4262	511.03	-1.776	0.650
084-04	C3	TPA2	AQ	C-C	6-31g(d)	-4.8472	-2.6082	2.2390	553.76	-1.892	0.347

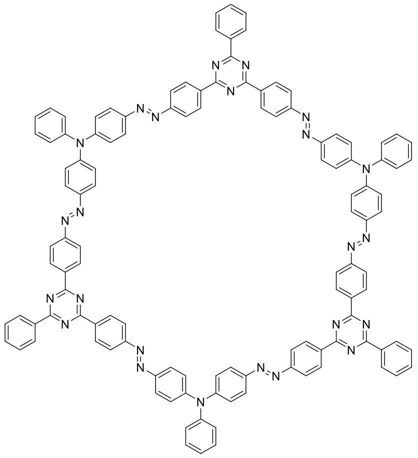

Figure 1. Structure of A07

References

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Valorisation of lignocellulosic biomass from post-consumer wast wood

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In recent decades the concepts of sustainability and in particular of circular economy have been discussed more frequently, aimed at developing economic and technological processes in order to minimize the impact and the quantity of waste and to maximize the recycling of products. This approach has gradually led to the use of natural resources and waste generated by anthropogenic production cycles. Among the most interesting waste, the biomasses lignocellulosic-based have a prominent position due to the huge availability from the human activities. The sources of these wastes derivate from the cleaning and the maintenance of parks or gardens, driftwood (wood deposited on the banks of water basins) and mowings of the undergrowth and post-consumer urban wooden waste.

In this work, we studied how to improve a technological process applied to post-consumer lignocellulosic-based waste, in order to obtain carbohydrates and substances that can be used in new chemical and biological transformation processes. to produce bio-based compounds and biofuels that can be an alternative to synthetic ones obtained from fossil sources such as oil. The treatment used, called Liquid Hot Water (LHW), is a hydrolysis process in which high temperatures and pressures are reached, with the purpose of destroying the material by opening its structure to transform into the organic substance into solution and then extract the sugars. The actions of hydrolysis are conducted by thermal approach, alkaline and acid environment, in which is required the addition in the aqueous solution of sodium hydroxide and sulfuric acid, respectively. At the end of each treatment step, two different phases are obtained: a solid one and a liquid one, on which various analysis are carried out as well as the characterization by HPLC.

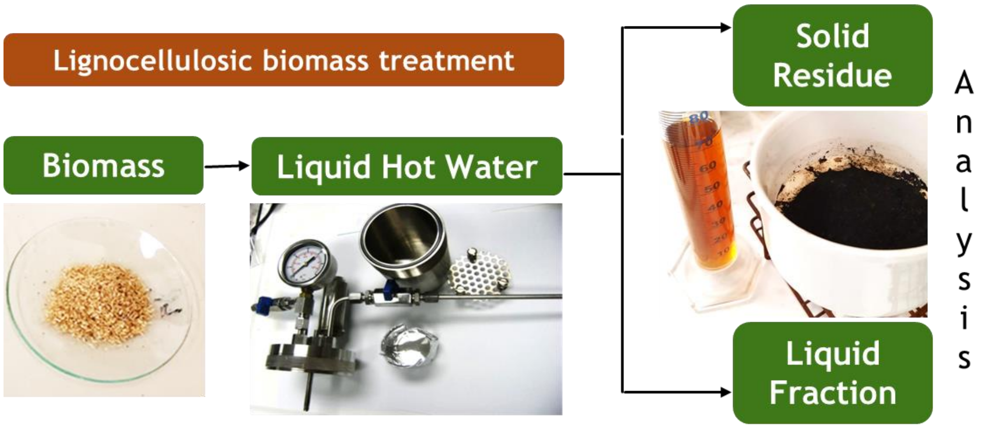

Figure 1. Scheme for hydrolysis treatment of post-consumer waste wood.

Biological nitrification process for ammonia removal in wastewater

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Ammonia-nitrogen, including non-ionized (NH_3) and ionized (NH_4^+), is a common pollutant in both municipal and industrial wastewater streams [1]. The presence of high concentrations of this contaminant is due to human activity and represent a risk for human health. In fact, World Health Organization (WHO), European environment agency (EEA) and local environmental authorities has recommended the limit of concentration of ammonia in water streams [2]. In this way, the study of economics and green methods for ammonia removal are important and fascinating for the researcher. An interesting option is the nitrification-denitrification process performed in biological reactors since the final product is N_2that that could be returned to atmosphere. Ammonia is oxidized in nitrite and nitrate by aerobic chemolitho-autotrophic bacteria during the nitrification. Then, in denitrification, the products of the first step are reduced to N_2 in anoxic environment by chemoorgano-heterotrophic denitrifying bacteria[3]. In the first part of the process the oxygen concentration inside the reactor is a critical parameter and the efficiency of the aeration system is relevant. In this way a purpose of this work is improve the mass transfer of oxygen to gas phase(air) to a liquid (wastewater) using membrane in order to sustain the oxygen demand of nitrification process. With the aim of performing the nitrification, batch reactors equipped with traditional, and membrane (built in lab) aerator were used. The tests were performed at 20°C using water prepared with ammonia concentration up to 500 ppm and a biomass of oxidation active sludge plant. During the nitrification ammonia was converted mainly into nitrites but also in nitrates. In all the system the concentration of oxygen was optimal and, using membranes, we can achieve higher oxygen concentration using lower air flowrates.

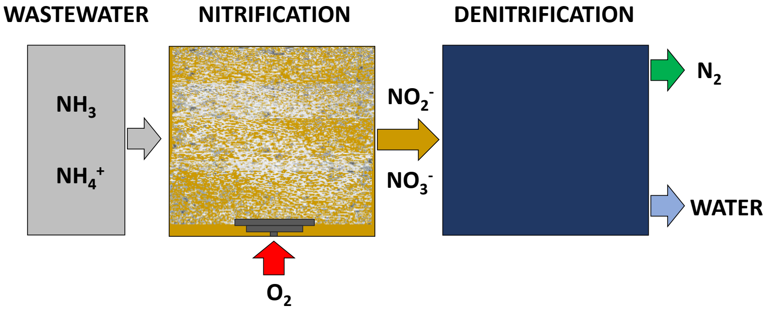

Figure 1. Nitrification-denitrification process scheme

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6. EDUCATION

Assessing the effectiveness of a systems thinking visualization tool implemented during a first-year chemistry intervention

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Within our current Anthropocene epoch, emerging global sustainability challenges call scientists from various disciplines to frame an action plan to address the environmental, social, and economic impacts that human activities have on our planet. In Chemistry, systems thinking provides a framework linking fundamental chemistry to human-environmental interactions and the sustainability agenda (Mahaffy, Matlin, Whalen, & Holme, 2019). Integrating systems thinking in chemistry education will equip students with the necessary skills to address sustainability challenges by reorienting the thinking and practice behind chemistry. Unfortunately, the lack of systems thinking in chemistry has led to an insufficient understanding of the primary activities of chemistry that contributed to irreversible impacts on societal systems and the environment (Mahaffy, Matlin, Holme, & MacKellar, 2019). Challenges that have contributed to the absence of systems thinking in chemistry education include the lack of consensus in the chemistry education community, limited systems thinking training, limited teaching resources and assessments, incompetent educators, and the potential cognitive overload caused by systems thinking (York & Orgill, 2020). To address the challenges associated with systems thinking in chemistry education, the Systems Thinking in Chemistry Education (STICE) framework is being developed by thought leaders in the discipline (refer to the special issue of JCE in 2019). Their goal is to enable a holistic approach to chemistry education that prepares citizens to partake in global sustainability with all their understanding of the systems involved. To this end, IUPAC funded two STICE projects focused on reorienting chemistry education by providing systems thinking resources, teaching materials, assessments, and support to educators to encourage the use of a systems thinking approach in chemistry education. (Mahaffy, Matlin, Holme, et al., 2019; Mahaffy, Matlin, Whalen, et al., 2019). In alignment with the goal of STICE, the proposed research project aims to implement a systems thinking intervention to develop systems thinking teaching materials and assessments to overcome barriers associated with a systems thinking teaching approach. In this project, a systems thinking visualization tool, known as a System- Oriented Concept Map Extension (SOCME) diagram, will be used in an intervention to develop systems thinking skills and to assess the extent to which systems thinking skills are applied using the SOLO taxonomy in a second semester first year chemistry module. Students will be required to use systems thinking skills to understand the chemistry of surfactants, in this case, alkylbenzene sulfonates, and to critically evaluate their impact on the various systems and subsystems of society, the environment, and the economy.

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7. HEALTH

DEVELOPMENT AND EVALUATION OF GREEN SOLID LIPID NANOPARTICULATE MOSQUITO REPELLENT CREAMS

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Introduction: The continuous and unrestricted use of pharmaceuticals such as pesticides, insecticides, and herbicides represents some of the leading causes of environmental pollution as these substances have been reported to cause adverse effects to various non-target organisms including humans. Hence, the need to design relevant technology for the manufacture of "greener pharmaceutical dosage forms" which will both have effective therapeutic action and still be eco-friendly.

Aim: The aim of the study was to develop and characterize solid lipid nanoparticulate (SLN) mosquito repellent creams containing oils from *Ocimum gratissimum* and *Azadirachta indica*.

Methods: The oils used for the study were obtained from the two plants by steam distillation. The various SLN batches were thereafter prepared using cold homogenization method. The stability of the formulated SLN creams was evaluated by measuring the pH, viscosity and particle size at various time intervals. In vitro occlusion test, skin irritation test, rheological studies, Fourier transform infra-red analysis (FTIR), encapsulation efficiency, loading capacity, ex vivo permeability and percentage repellence for the SLN batches were also determined.

Results: The study showed a significant decrease in the pH values and viscosities of the various formulations and an increase in particle size. The formulations showed higher occlusive effect and higher permeation coefficients compared to the commercial 12 % DEET cream (Odomos®) and no sign of skin irritation. The principal peaks of FTIR spectrum of the plant extracts and the plain SLN appeared in the various formulation batches. The encapsulation efficiency values of the SLN batches were between 52 % and 88 %, while loading capacity values of the various batches were between 2.6 % and 13.3 %. The rheological characterization showed that the batches exhibit dominant solid-like behaviour between 4 ˚C and 40 ˚C and that above 40 ˚C there was an increase in the liquid-like behaviour of the systems. The control (12 % DEET) produced significantly higher percentage mosquito repellence compared to the SLN creams. However, the SLN formulations produced higher repellence than the unformulated oils.

Conclusion: This study showed the performance of the SLN formulations as a possible candidate for the delivery of botanical extracts for mosquito repellent application.

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Analysis of *N*-nitrosamines in South African waters by LC−MS/MS and the comparison of extraction techniques employed

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Chlorination and chloramination are the most widely used disinfection treatments, some water treatment plants (WTPs) employ chloramination due to it being able to reduce levels of ubiquitous disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) [1]. However, this disinfection treatment produces high levels of nitrogenous DBPs, in particular nitrosamines such as *N*-nitrosodimethylamine (NDMA) [2]. Nitrosamines are considered highly carcinogenic and genotoxic compounds [2, 3]. The most prevalent method to analyze nitrosamines in water is solid-phase extraction (SPE) coupled with gas chromatography-mass spectrometry (GC− MS) or liquid chromatography-mass spectrometry (LC−MS) [2]. The use of GC precludes the analysis of non-volatile or thermally unstable nitrosamines, as they decompose in the GC injector [2, 4]. LC−MS can analyze thermally-unstable/ non-volatile nitrosamines and/ or higher molecular weight nitrosamines that may be formed during the disinfection process that cannot be analyzed by GC− MS [4]. This renders LC−MS a good candidate to identify nitrosamines that are not yet known. During the monitoring of environmental pollutants, it is always of paramount importance that green analytical chemistry principles are adhered to [5]. Two extraction methods will be explored and their efficacies will be compared against each other, namely SPE and molecularly imprinted polymers (MIPs). Traditional methods used on the synthesis of MIPs still require large amounts of organic solvents, however, there have been techniques devised to circumvent this [6]. Supercritical carbon dioxide (SCD), ionic liquids, and ultrasound technology are some of the green strategies which have been already applied in the synthesis of MIPs. For this particular research, the use of SCD in the synthesis of MIPs will be explored as this technique has several advantages, such as being inexpensive, non-toxic, non-flammable, inert, odorless, easily removed without any additional energy input, and can be recycled [6].

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STUDY OF TOXICITY AND CELLULAR UPTAKE OF MAGNETIC NANOPARTICLES WITH DIFFERENT COATINGS

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Currently, magnetite nanoparticles (MNP) are widely studied for their possible applications in numerous biotechnological fields, such as separation and recycling, (bio) detection, (bio) catalysis, and also in the biomedical area. Their biocompatibility, relatively low toxicity, superparamagnetism (in a size range of 10-20 nm), and versatility for surface modification make these nanomaterials suitable for the areas mentioned above [1]. Nanoparticles' high surface/volume ratio allows incorporating a large number of molecules, which give them colloidal stability, biorecognition specificity and modulate their interaction with proteins and cell membranes [2]. In the context of biotechnological application, it is necessary to analyze the interactions between MNP and cells; however, there are relatively few studies that correlate the physicochemical properties of these nanomaterials and their influence on cell interactions and the toxic effect that they can produce. In order to carry out the functionalization of nanoparticles with biomolecules (carbohydrates or proteins) that will act as a recognition element for sensing, an accessible surface chemistry is necessary. In this work, we synthesized pristine magnetite nanoparticles (MNPs) and magnetite nanoparticles functionalized with the chemical groups, amino (MNP-Ar-NH_2) and carboxylic acid (MNP-Ar-COOH). The nanoparticles were characterized to stablish the size, surface coverage, charge and zeta potential. The cytotoxicity and cellular uptake of each type of nanoparticles were compared. For this purpose, Chinese hamster ovary (CHO- K1) cells were used as a model to assess cellular viability by using the Alamar Blue reagent. In the range evaluated, up to 0,5 mg/mL, nanoparticles did not significantly affect cell viability. Cell uptake studies were performed by confocal microscopy on HeLa cells which stably expressed the autophagic protein LC3B fused to the green fluorescent protein (GFP). The results obtained showed a higher internalization of MNP-Ar-NH_2 compared to MNPs and MNP-Ar-COOH. Moreover, we observed an increase in LC3B (+) vacuoles which correlates with an activation of autophagy to promote MNPs degradation. This reveal how the initial surface properties of nanoparticles conditioned the interactions with the components of the culture media, represented mainly by proteins, and this is extrapolated to the interaction with cells. It is well known that the protein corona changes the chemical identity of the nanoparticles, therefore when the cellular uptake occurs the dynamic of internalization might be different to each nanoparticle.

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Target Identification for Antimalarial Natural Products

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Malaria is a life-threatening disease commonly in the Sub-Saharan Africa as a result of the dominating most deadly malaria parasite, the *Plasmodium falciparum*. The parasite has become resistant to available antimalarial drugs due to its ability to spontaneously mutate thereby affecting the structure and activity of the drug [1]. The situation necessitates researchers to identify new drug targets in distinct biosynthetic pathways of the malaria parasite for the design of efficient antimalarial drugs. Herein, machine learning tools are used to identify novel *Plasmodium falciparum* targets for the available Natural Products antimalarial hits. From biological databases, *Plasmodium falciparum* targets data is extracted and filtered using Naïve Bayesian, targets are predicted through the Systems approach and the potential target is identified by reading through the patterns within genomic data of the critical targets [2]. From a tree found in Zimbabwe, the antimalarial actives are extracted using the relevant solvents, isolated and characterized. Antimalarial activity, phytochemical screening, chromatography and structure determining techniques like NMR and FTIR were carried out [3]. The structures are then downloaded from the DrugBank database and docked against the potential targets to select the top ligand-target interaction using the scoring criteria [4]. New interactions discovered may lead to the discovery and development of a new antimalarial drug that is able to inhibit the parasite from mutating and resisting the drug. Computational methods give assurance of the relevant interactions of a compound to its target before further experimental work is carried out [5]. This project answers the Green Chemistry principle number 4 of designing safer chemicals because toxicity of drugs can be tested computationally before its synthesis.

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Incorporation of *Pelargonium Alchemilloides (L). L'Herit* Extracts Into Polyvinylpyrrolidone/Cellulose acetate Blended Fibres and Their Antibacterial Activity

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The continuance of antibiotic high resistance in pathogens is still a big threat to fragile people and critically ill hospital patients. Infections caused by bacteria might cause severe damages to human health including death and, hence, reduce the success of medical advancements, among others: treatment of chronic wounds and medical implants. Hence, it is very crucial to develop novel materials that will accurately deliver new antibiotics and uptake pathogenic microbes. The project explores the effectiveness of electrospun nanofibers as the solution to some of the concerns. This includes a report on the use of electrospinning to encapsulate *Pelargonium Alchemilloides (L). L'Herit (P.A)* extract in nanofibrous mats. Polyvinylpyrrolidone and cellulose acetate are the building blocks of the composite fibers that will serve as the hydrophilic matrix to incorporate the extract mainly to improve the biological activity of the composite fibers. First, *Pelargonium alchemilloides (L). L'herit* extract as natural and antimicrobial agent (with different concentrations) are incorporated into polyvinylpyrrolidone (PVP)/cellulose acetate (CA) blended solution, aiming to produce nanofibers with a uniform and bead-free morphology. Afterward, the influence of plant extract and processing parameters on the morphology of the electrospun blend nanofibers are investigated using different analytical techniques. Finally, the biological activity includes test of their activity against selected bacteria found in chronic wounds, among others: the gram-negative bacteria *Escherichia coli (E. coli)* and gram-positive bacteria *Staphylococcus aureus (S. aureus)*.

Keywords: Electrospun nanofibers, *Pelargonium alchemilloides (L). L'herit*, polyvinylpyrrolidone (PVP)/cellulose acetate (CA) blend solution, *Escherichia coli*, and *Staphylococcus aureus*.

Directed formation of polymorphs of furosemide via inclusion compounds

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The ability of a compound to crystallise in different crystalline forms is called polymorphism [1]. In the pharmaceutical industry, polymorphism is important because the properties of the different polymorphs may vary, and these subtle differences subsequently influence the applicability of the active pharmaceutical ingredient in solid-state formulations. For this reason, it is essential to understand how to obtain the preferred polymorph of a drug under given conditions, but this process is far from being straightforward in practice [2]. A possible route to obtain polymorphs is (i) to form the solvate of the compound of interest and then (ii) enforce desolvation with the hope that the desolvated product will result in the desired polymorph [3].

In this study, furosemide, (4-chloro-2-[(2-furanylmethyl)-amino]-5-sulfamoylbenzoic acid), a loop diuretic with acidic nature (Figure 1) was used to form various inclusion compounds with heterocyclic bases (pyridine and its derivatives). The selected coformers have complementary functional groups to increase the possibility of forming hydrogen bonds between furosemide and the coformers and subsequently increase the likelihood of the formation of solvate inclusions. The selected coformers also have low boiling points, thus the desolvation of the inclusion crystals could be carried out at ambient temperature. This is a crucial step to consider when this experimental route is used because transformation between polymorphs can be easily triggered by energetic processes. The X-ray crystal structures of four solvates, their general analytical data (TGA, FTIR, XRD, and DSC) are presented, and the results of the desolvation experiments will be discussed.

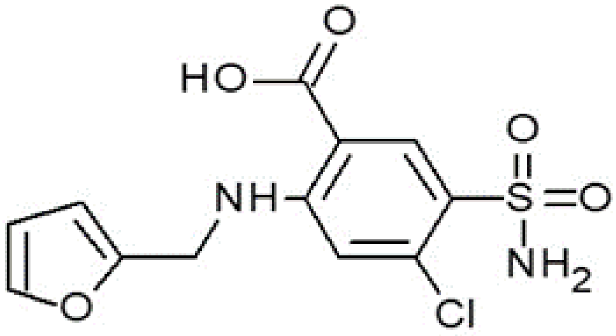

Figure 1. Molecular structure of furosemide (FUR)

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Phytochemical, Pharmacognostic, Antimicrobial and Antiulcer studies of *Vitex doniana* (Lamiaceae) Leaf and Stem bark

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Phytochemicals in plants have diversified the application of various plants, whether edible or not, as Nutraceuticals or Therapeutics. These have been found to be relatively cheaper, better affordable and safer than modern/synthetic medicines. Pharmacognostic studies are carried out on plant drugs, crude or standardized, to facilitate quality control. *Vitex doniana* is a tropical tree of the family Lamiaceae, with various applications, from the edible young leaves to the sweet fruit pulp, ethnomedicinally used to remedy various diseases of the GIT including peptic ulcer.

Leaf and stem bark samples of *Vitex doniana* were evaluated for basic Pharmacognostic standards viz. macroscopical, microscopical, chemomicroscopical analysis, and physicochemical analysis; cold maceration and liquid-liquid partitioning was used to obtain a methanol crude extract, and fractions of n-hexane, ethylacetate, and methanol. These were then evaluated for the presence of basic phytochemicals, acute toxicity studies, antimicrobial sensitivity (agar well diffusion method) with Gentamicin and Fluconacol as reference. Also, anti-ulcer studies in rats using the ethanol and Cimetidine model. Data obtained were statistically analyzed using the IBM SPSS Statistics 21 software.

Results were anomocytic stomata, dorsoventral leaf with glandular, multicellular and unicellular trichomes. The stem bark had various fibrous cellular contents. Phytochemicals found were alkaloids, flavonoids, tannins, saponins, steroids, and carbohydrates. The plant samples exhibited significant ($p < 0.05$) antimicrobial activity with an MIC of 50 mg/mL. Similarly, ulcer preventive activity was profound with at least 88.9 % ulcer inhibition at 600 mg/Kg. LD_{50} was > 5000 mg/Kg (Lorke's method). *Vitex doniana* is therefore a good drug candidate for antiulcer and antimicrobial use; and is relatively safe for consumption. The presence of the phytochemicals may have formed a synergistic or additive effect for a successful treatment of ulcer as opposed to the limited management of peptic ulcer by orthodox drugs.

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EXPOSURE PATHWAYS AND HEALTH RISKS OF POLYBROMINATED DIPHENYL ETHERS IN DUST FROM CHILDREN FACILITIES IN NSUKKA, ENUGU STATE

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The determination of Polybrominated diphenyl ethers (PBDEs) in dust from crèches and nursery schools in Nsukka, Enugu state was carried out. The health risks to toddlers, children and adults in both children facilities via inhalation, ingestion and dermal exposure pathways were evaluated. Sampling of dust was carried out on a weekly basis over a period of one month (July 2019) from ten crèches and nursery schools. Thirty samples were obtained from all the facilities. Control samples were also obtained from an unfurnished room. The samples were extracted by ultrasonication using n-hexane and acetone in the ratio 1:1 and recovery analysis was carried out. Eight PBDEs congeners: 2,4,4'-Tribromodiphenyl ether (BDE 28), 2,2',4,4'-Tetrabromodiphenyl ether (BDE 47), 2,2',4,4',6-Pentabromodiphenyl ethers (BDE 100), 2,2',4,4',5-Pentabromodiphenyl ether (BDE 99), 2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE 154), 2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE 153), 2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE 183) and 2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE 209) were determined using Gas Chromatography - Mass Spectrometry. The average recovery of PBDEs in the dust samples ranged from 80 to 108%. The concentrations (mg/kg) of PBDEs ranged from 0.017 ± 0.010 to 8.560 ± 0.001 in crèches with a mean of 0.664 and 0.016 ± 0.003 to 2.463 ± 0.183 in nursery with a mean of 1.109. The concentrations of PBDEs decreased in the following order: BDE 99 > BDE 154 > BDE 47 > BDE 100 > BDE 183 > BDE 153 > BDE 28 > BDE 209 for crèches and BDE 99 > BDE 28 > BDE 47 > BDE 100 > BDE 183 > BDE 154 > BDE 153 > BDE 209 for nursery schools. There was a significant difference ($p<0.05$) between the concentrations of PBDEs in both children facilities. Principal component analysis result showed that the PBDEs in crèches were from the commercial mixtures of pentaBDEs (DE-71) and decaBDE (Saytex 102E) while those in nursery schools were from octaBDE (DE-79) and pentaBDEs (DE-71) respectively. Dust ingestion was found to be the predominant exposure pathway for toddlers (82%) and children (76%) while dermal absorption was found to be the dominant pathway through which adults (93%) in both facilities were exposed to PBDEs. The hazard indices of all the exposure pathways for toddlers, children and adults in both facilities were less than 1.0 signifying that there was no health risk. The analytical eco-scale assessment showed that the method is an acceptable green analytical method which is environmentally friendly.

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Antischistosomal Structure-activity Relationship of Pyridazinylbenzamides

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Schistosomiasis is a water-based parasitic disease that affects over 250 million people. Control efforts have long been in vain, which is one reason why schistosomiasis is considered a neglected tropical disease (NTD). However, since the new millennium, interventions against schistosomiasis are escalating. The initial impetus stems from a 2001 World Health Assembly resolution, urging member states to scale-up deworming of school-aged children with the anthelminthic drug praziquantel. With the recent publication of the World Health Organization (WHO) Roadmap to overcome the impact of NTDs in 2020, we have entered a new era. The major approach used for disease control and treatment is chemotherapy, using Praziquantel (PZQ) which has been in use for half a century. PZQ is safe, efficacious and inexpensive. However, with respect to eliminating adult worms, PZQ is only partially efficacious. It is not effective on young worms, and does not prevent reinfection. Moreover, drug resistant strains of the parasite have been documented in endemic areas such as Kenya and Egypt, a situation which is compromising the efficacy of PZQ in managing schistosomiasis. The emergence of worm strains less sensitive to PZQ and the over reliance on praziquantel have presented the urgent need for *novo* antischistosomal drugs that are cheaper and more efficacious. This study, therefore proposes the synthesis and evaluation of *in vitro* antischistosomal bioactivity and structure-activity relationships (SARs) of *pyridazinylbenzamide* analogues, the most bioactive of which will be evaluated *in vivo* in mice infected with *Schistosoma mansoni*, a species common in Zambia[1,2]. Furthermore, the most bioactive analogues will undergo pharmacokinetic studies.

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Rational Synthesis of Three-dimensional Core-double Shell Upconversion Nanodendrites with Ultrabright Luminescence for Bioimaging Application

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Engineering the morphology of rare-earth doped $NaYF_4$-based upconversion nanoparticles (UCNPs) can effectively tune their upconversion luminescence emissions (UCLE) properties. Herein, we rationally synthesized a new class of three-dimensional upconversion core-double-shell nanodendrites (UCNDs) including an active core ($NaYF_4$: Yb, Er, Ca) capped by a transition layer ($NaYF_4$: Yb, Ca) and an active outer shell ($NaNdF_4$: Yb, Ca). The high concentration of Nd^{3+} sensitizer in the outer dendritic shell enhances the luminescence intensity, while the transition layer enriched with Yb^{3+} acts as an efficient energy migration network between the outer shell and inner core along with preventing the undesired quenching effects resulting from Nd^{3+}. These unique structural and compositional merits enhanced the UCLE of UCNDs by 5 and 15 times relative to $NaYF_4$: Yb, Er, Ca@$NaYF_4$: Yb, Ca truncated core-shell UCNPs and $NaYF_4$: Yb, Er, Ca spherical core UCNPs, respectively under excitation at 980 nm. The SiO_2-COOH layer coated UCNDs (UCND@SiO_2-COOH) were successfully used as efficient long-term luminescence probes for the *in vitro* and *in vivo* bioimaging without any significant toxicity. The uptake and retention of UCND@SiO_2-COOH were almost found in the liver and spleen. This study may open the way towards preparation of spatial UCNDs nanostructures for biomedical applications.

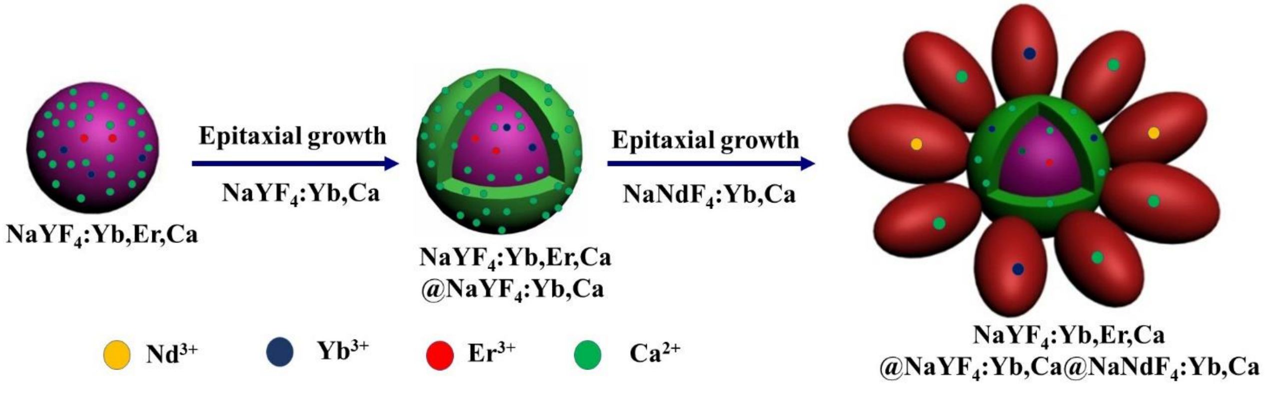

Figure 1. The fabrication process of UCNDs.

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Photorheometric Study of Vanillin Acrylate-based Resins and Antimicrobial Properties of Polymers

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Vanillin produced by chemical modification of lignin is considered as natural vanillin and is 250 times cheaper than synthetic vanillin. Due to aromatic structure it could be able to replace widely used petro-based aromatic monomers [1]. Photopolymerization engendered high interest both in academia and in industry due to the considerable practical and economic benefits. Advantages of the photopolymerization are following: high reaction speed, low energy consumption, high efficiency, low volatile organic compound emission, and the large number of applications in not only conventional areas such as coatings, inks, and adhesives, but also in high-tech domains, such as microelectronics, optoelectronics, laser imaging, stereolithography, and nanotechnology [2-3].

The investigation of the influence of vanillin acrylate-based resin composition on photocuring kinetics, swelling values, yield of insoluble fraction and antimicrobial properties of the resulting polymers was performed in order to find efficient photocurable system for optical 3D printing of bio-based polymers. Two vanillin derivatives, vanillin diacrylate and vanillin dimethacrylate, were tested in photocurable systems with 1 mol of 1.3-benzenedithiol or without it, using bis(2,4,6-trimethylbenzoyl)phosphine oxide as photoinitiator.

The photocuring kinetics of vanillin acrylate-based resins was investigated by real-time photorheometry. The addition of thiol into the resin increased the photocuring rate but reduced the rigidity of obtained polymers while the addition of solvent reduced photocuring rate and rigidity. Vanillin dimethacrylate-based polymers demonstrated a higher yield of insoluble fraction and lower swelling values in acetone and toluene. Vanillin acrylate- and vanillin methacrylate-based polymers showed antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. Toxicity to the microscopic fungus *Aspergillus niger* and *Aspergillus terreus* was less pronounced.

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Extraction of astaxanthin from *Haematococcus pluvialis* with hydrophobic deep eutectic solvents

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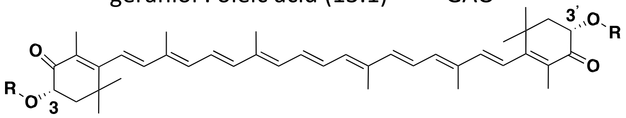
Astaxanthin (3,3′-dihydroxy-β,β-carotene-4,4′-dione) is the most powerful antioxidant natural carotenoid and has excellent anti-inflammatory and anticancer properties. *Haematococcus pluvialis*, a green microalgae, is one of the main sources of natural astaxanthin (1-5% dry weight of biomass). Under stressful conditions, such as high-intensity light irradiation and lack of nutrients, *H. pluvialis* shifts from a vegetative green phase into a quiescent red phase, in which astaxanthin is accumulated. The red phase has very thick and rigid cell walls, which complicate the extraction process[1]. Different extraction methods have been applied (ultrasonic, microwave or supercritical fluid-assisted), and the use of hydrophobic deep eutectic solvents in this context can represent a valid alternative[2]. They are new generation solvents composed by a mixture of two or more substances, liquid at room temperature, immiscible with water. They are non-volatile, so the extract is no more separable from the solvent, but they can be used to preserve and enhance the bioactivity of the extracted compound.

DES (molar ratio)	acronym
menthol : oleic acid (2:1)	MAO
thymol : oleic acid (3:1)	TAO
geraniol : oleic acid (13:1)	GAO



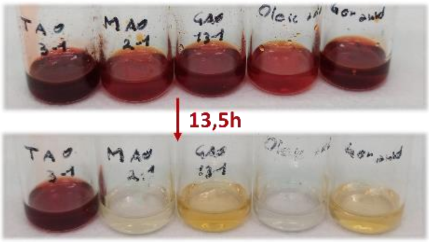


Figure 1. Extraction and stability of astaxanthin in hydrophobic DES

Hydrophobic DESs were prepared and tested on both freeze-dried biomass and *H. pluvialis* cultures exploiting their high affinity for hydrophobic molecules such as astaxanthin and their extraction kinetics and abilities were evaluated, **Figure 1** (characterisation and quantification were perferomed by HPLCUV/Vis analysis). Because of its well-known instability, astaxanthin tends to easily degrade due to heat, oxygen and light exposure. The potential of DES to stabilize astaxanthin in the extracts was therefore evaluated under controlled "aging" conditions (light and time). The solvent composed by thymol and oleic acid (3:1), TAO, demonstrated great extraction ability and enhanced considerably astaxanthin stability. This system can therefore be considered a THEDES, therapeutic DES[3].

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Fully renewable NIPUs *via* thiol-ene polymerization

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Polyurethanes (PU) are one of the most important class of polymeric materials, with applications ranging from insulation panels and foams to high performance adhesives and fibres. Industrially, PUs are synthesized by polyaddition of isocyanates with diols. Isocyanates have been not only been confirmed to be harmful for humans, but are also produced using highly toxic phosgene and amines. An alternative procedure toward PUs is therefore of utmost importance.

In this work, we present a different approach, in which the urethane monomer is prepared *via* the Lossen rearrangement [1] in a one-step synthesis and polymerized with both sustainable and commercially available dithiols to produce a polyurethane chain with thioether linkages. The advantages of this method lie not only in the sustainable design during the preparation of the carbamate functionality, in the tunability of polymer properties by choice of dithiol moiety and the employment of the urea side-product, but also in the possibility to prepare block- and random copolymers with interesting thermal and mechanical properties.

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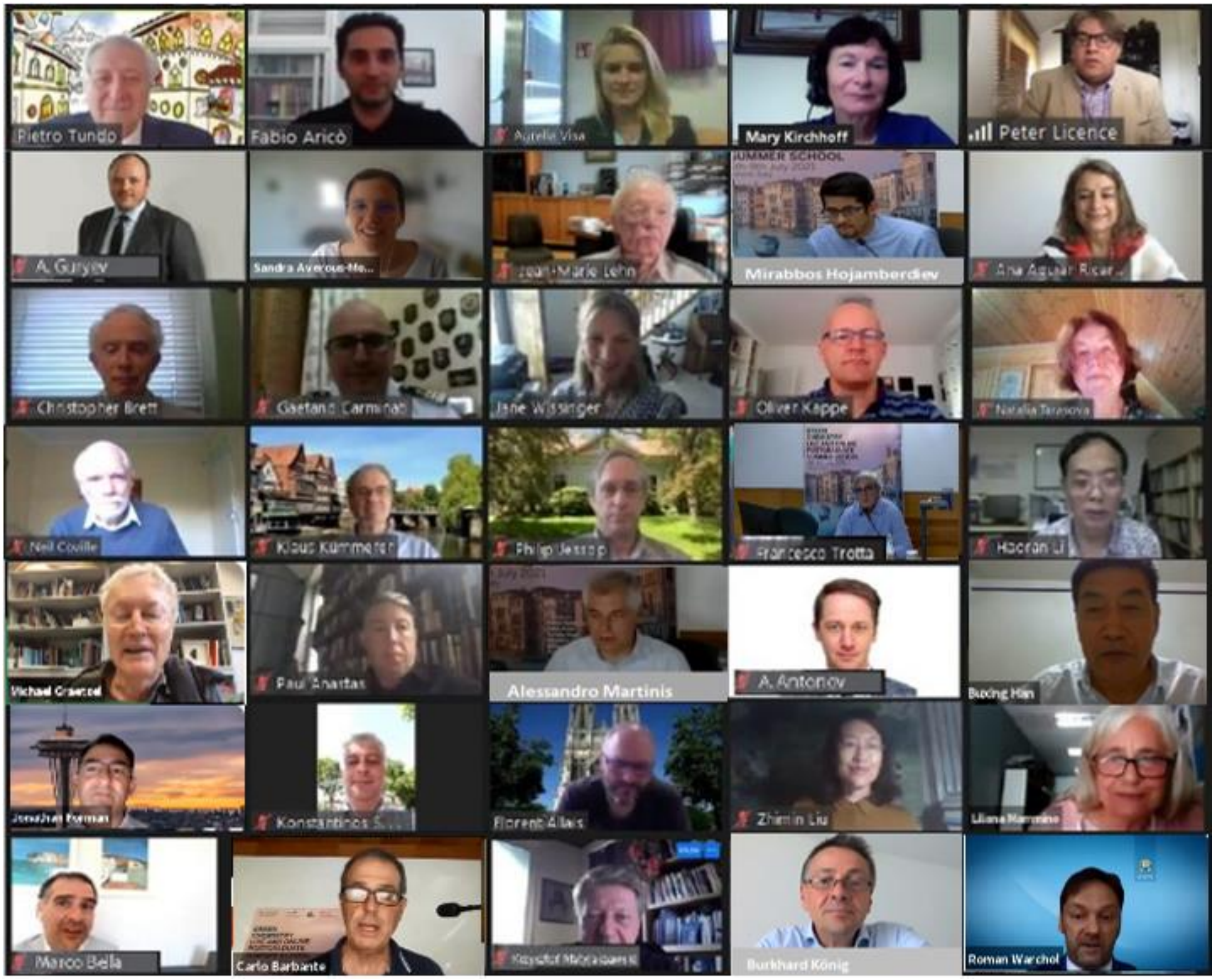

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