

PROCEEDINGS

of the

14th Green Chemistry Postgraduate Summer School

(online/in-person)

3-8 July 2022, Venice, Italy



**Green Sciences For Sustainable
Development Foundation**

COLLECTION OF ABSTRACTS

Editors: Mirabbos Hojamberdiev, Fabio Aricò, Aurelia Visa and Pietro Tundo
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3-8 JULY, 2022 – ONLINE/IN-PERSON



GREEN CHEMISTRY LIVE AND ONLINE POSTGRADUATE SUMMER SCHOOL

3rd-8th July 2022
Venice, Italy

Organizers:
Pietro Tundo Chairman
Fabio Aricò
Aurelia Visa
Mirabbos Hojamberdiev
Graziana Gigliuto Secretary
Alessandra Abbate Assistant Organizer

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

Info:
www.greenchemistry.school
www.gssd-foundation.org

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green.chemistry@unive.it

sponsors



3-8 JULY, 2022 – ONLINE/IN-PERSON

The Editors would like to thank Graziana Gigliuto and Alessandra Abbate for their wonderful support in the creation of this book.

**PROCEEDINGS of the
14th Green Chemistry Postgraduate
Summer School (online/in-person),**

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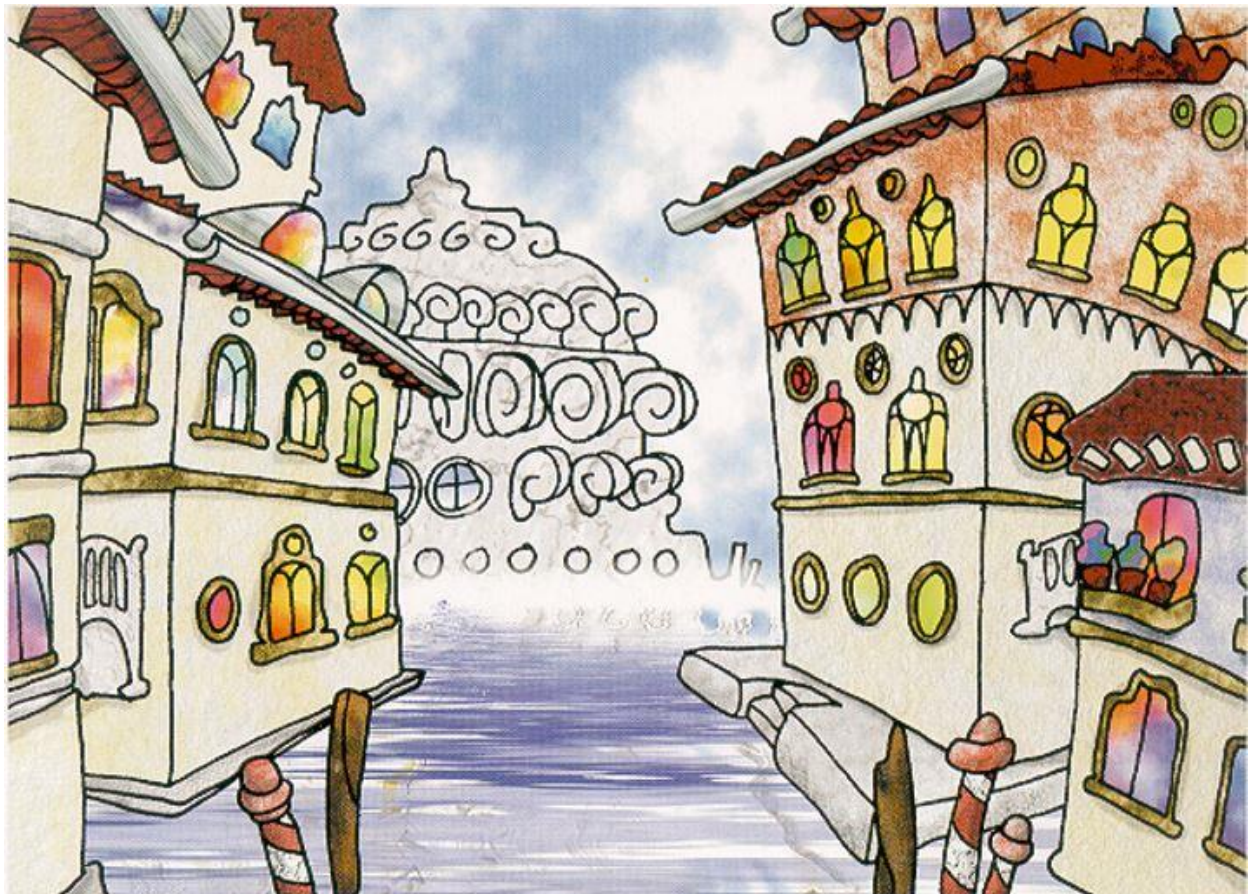


JULY 3-8, 2022 – ONLINE/IN-PERSON



GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

*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.*



JULY 3-8, 2022 – ONLINE/IN-PERSON

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

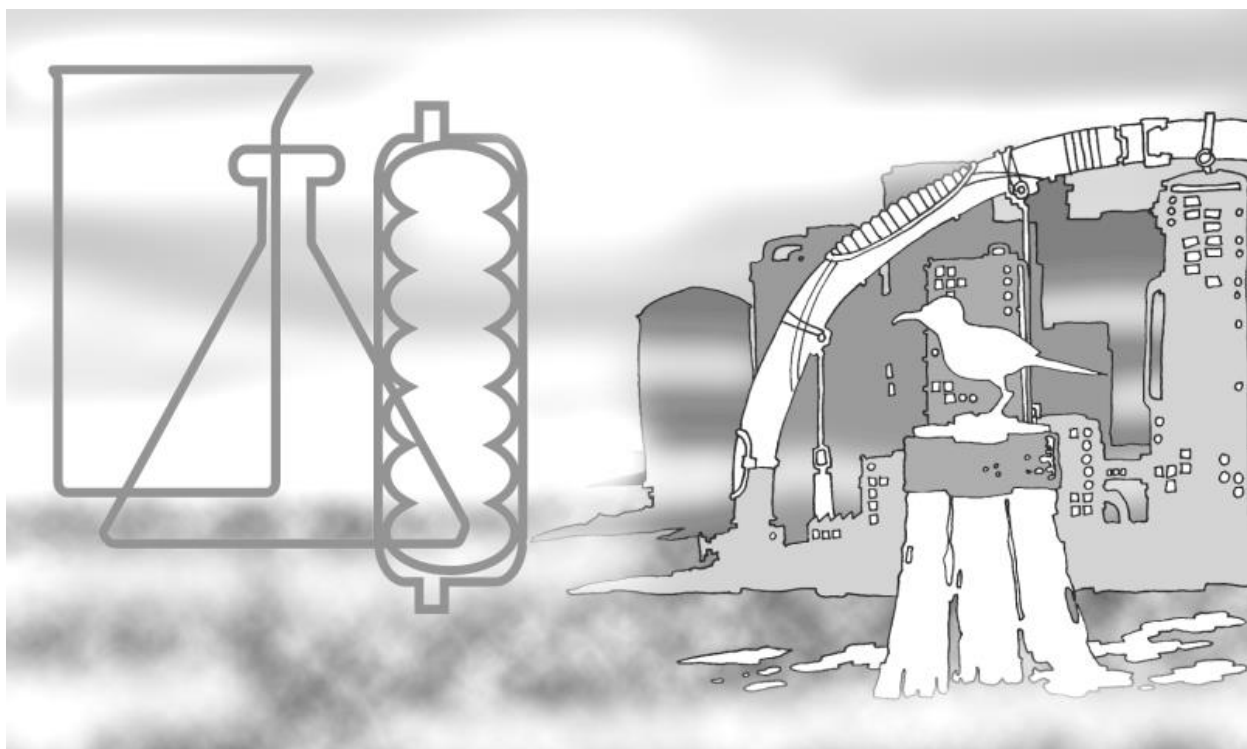
Main aims of the Foundation are:

- 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.



JULY 3-8, 2022 – ONLINE/IN-PERSON

GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL
3rd-8th JULY 2022, ONLINE/IN-PERSON

BOOK OF ABSTRACTS

CONTENTS

Welcome Message from the Chair of the Summer School	2
Foreword by one of the Rector Delegates Ca' Foscari DAIS.....	4
Foreword by the Standing Committee Chair ICGCSD IUPAC	5
Summer School Committees	6
Lectures & Teachers	8
Timetable	10
Programme	11
Summer School Topics	16
Teachers' Lecture Abstracts	17
Students' Abstracts	45
1. New reaction pathways.....	56
2. Exploitation of renewable resources	92
3. Energy saving	122
4. Health	145
5. Food safety	168
6. Climate Change damages mitigation.....	173
Group Photo	189

WELCOME MESSAGE FROM THE CHAIR OF THE SUMMER SCHOOL



Dear Ladies, Gentlemen, Students, Friends and Colleagues,

I am Pietro Tundo, 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 is held online and onsite; the 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, PhosAgro. Yale University, Sasol, Nhu China, Bracco Foundation and GreeNovator. Moreover, this Summer School has obtained the endorsement from UNESCO Roma, from Italian Council of Researches, from IUPAC, from Ministero della Transizione Ecologica, from Veneto Region, from the Municipality of Venice, from Ca' Foscari University, International Year of Basic Sciences for Sustainable Development 2022 and International Younger Chemists Network.

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 students 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 (8 scientific sessions) and, not less important, through the 10 poster sessions, both online and in person. So, the programme is very rich and intensive, and we hope to meet the expectations of such many students.

The peculiarity of this Summer School is not only to give updates regarding the advances in the Green Chemistry research year by year, but also to grant the attendance of meritorious students coming from developing countries and actively involve them as actors of the School. Thanks to the Sponsors financial support, students from all over the world had a unique opportunity to participate in person in the work of the School and to contribute to the development of current research and to establish peaceful relationships among them which will last long their lives.

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.

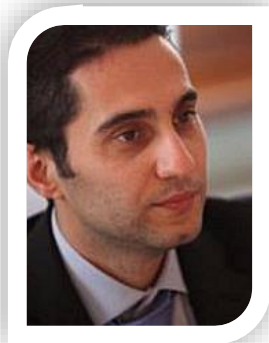
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Green Chemistry is a future-oriented approach to reconcile and foster the research in the chemical sciences with society and its needs. So, we necessitate as many as possible new and surprising proposals coming from pure and applied research, in order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

Pietro Tundo

Chair of the Summer School

**FOREWORD BY ONE OF THE RECTOR DELEGATES FOR INTERNATIONALIZATION
OF CA' FOSCARI DAIS**



As one of the Rector's Delegates for Internationalization 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 live and also online, from July 3 to 8 2022.

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

According to the CENSIS 2022 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 is the third time that Ca' Foscari has reached this achievement as a 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.

The 2022 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 (more than 90!) 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.

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.

Fabio Aricò

Rector Delegate to Erasmus and Overseas Agreements

Department's Delegate for Internationalization

Professor of Organic Chemistry Ca' Foscari University,

Organizing Committee of the Green Chemistry Postgraduate Summer School 2022

FOREWORD BY STANDING COMMITTEE CHAIR ICGCSD IUPAC



The 14th Green Chemistry Postgraduate Summer School was successfully held in Venice from 3rd to 8th, July 2022, which was organized and managed by the Green Sciences for Sustainable Development Foundation (GSSDF) in Venice, Italy. The Summer School was chaired by Prof. Pietro Tundo, President of Green Sciences for Sustainable Development Foundation, who is also the former Chair of The Interdivisional Committee on Green Chemistry for Sustainable Development (ICGCSD), IUPAC. The Organizing Committee also included Prof. Fabio Aricó from Ca' Foscari University of Venice, Italy, Dr. Aurelia Visa from Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry in Timisoara,

Romania, and Associate member of ICGCSD, Dr. Mirabbos Hojamberdiev from Institut für Chemie, Technische Universität Berlin, Germany, Ms. Graziana Gigliuto, Secretary and Ms. Alessandra Abbate, Assistant Organizer from GSSDF. 161 students from 45 countries attended the Summer School. In fact, the green chemistry summer schools of the 13 previous ones organized by Professor Tundo and his colleagues were also very successful.

Green chemistry, which can be defined as the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances, is very important for the sustainable development of our society. Although it has developed quickly in the past 30 years, it is still in the early stage. Development of green chemistry is a long-term task. Young students will play a key role in the development of green chemistry in the future. Therefore, it is no doubt that the summer school is an important event in the field of green chemistry now and for the future. I hope this series of summer schools will be held continuously in the future.

It is a great pleasure for ICGCSD to be a sponsor of the summer school. On behalf of ICGCSD, I would like to congratulate the great success of the summer school.

Buxing Han

Standing Committee Chair Interdivisional Committee on Green Chemistry for Sustainable Development (ICGCSD) IUPAC

JULY 3-8, 2022 – ONLINE/IN-PERSON

SUMMER SCHOOL COMMITTEES

CHAIR OF THE SUMMER SCHOOL

- **Pietro Tundo**, *Secretary 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*
- **Graziana Gigliuto**, *Green Sciences for Sustainable Development Foundation, Italy*
- **Alessandra Abbate**, *Green Sciences for Sustainable Development Foundation, 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*
- **Natalia Tarasova**, *Director, Institute of Chemistry and Problems of Sustainable Development, Mendeleev University of Chemical Technology of Russia; Corresponding Member of the Russian Academy of Sciences-Russia.*

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*

JULY 3-8, 2022 – ONLINE/IN-PERSON

- **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*

JULY 3-8, 2022 – ONLINE/IN-PERSON

PLENARY LECTURES

JEAN-MARIE LEHN

ISIS, Université de Strasbourg, France

Perspectives in Chemistry: Molecular – Supramolecular – Adaptive Chemistry

PIETRO R. TUNDO

Institute of Chemistry of Organometallic Compounds – ICCOM, National Research Council – CNR and Green Sciences for Sustainable Development Foundation, Venice

Reaction Mechanisms and Gibbs 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 (EPFL), 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

JULY 3-8, 2022 – ONLINE/IN-PERSON

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

Center for Green Chemistry and Green Engineering, Yale University, New Haven, CT 06520, United States

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 Sempredoni 5, Negrar (Vr), Italy

Green Radiochemistry: Dream or Reality?

VITTORIO ESPOSITO

ARPA Puglia, Environment Agency of Apulia, Italy

Command-and-Control vs Pollution Prevention in Environmental Policies for Achieving Green and Sustainable Steel Production in Italy- Case Study Taranto

JONATHAN E. FORMAN

Science and Technology Advisor, Global Security Technology and Policy, Pacific Northwest National Laboratory, Seattle, WA 98109 USA

Chemicals of War and Peace: Arms Control, Disarmament, Non-Proliferation, and Green Chemistry?

BUXING HAN

Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, China; Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

Conversion of CO₂ and Biomass into Chemicals and Fuels

MIRABBOS HOJAMBERDIEV

Uzbekistan-Japan Innovation Center of Youth, Tashkent 100095, Uzbekistan

Institut für Chemie, Technische Universität Berlin, Germany

Perovskite BaTaO₂N for Green Hydrogen Generation from Solar Water Splitting

C. OLIVER KAPPE

Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria

Going with the Flow – The Use of Continuous Processing in Organic Synthesis

ALEXEI LAPKIN

Department of Chemical Engineering and Biotechnology, University of Cambridge, United Kingdom

Artificial Intelligence Tools for Developing Greener Chemical Solutions

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

MARTIN MÖLLER

DWI - Leibniz Institute for Interactive Materials, Aachen, Germany

The Innovation Potential of Bioinspired Materials

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*

Adding Value to Biorefinery and Pulp Industry Side-streams: Lignin Valorization to Fuels, Chemicals and Polymers

FRANCESCO TROTTA

Department of Chemistry, University of Turin. Via Pietro Giuria 7, 10125 Torino - Italy

Exploitation of Renewable Resources in Polymer Chemistry

AURELIA VISA

Institute of Chemistry “Coriolan Dragulescu”, 24 M. Viteazul Ave, Timișoara - 300223, Romania

Metal Organic Frameworks: Complexity and Diversity in Structures and Green Applications

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

14th Green Chemistry Postgraduate Summer School Timetable
3rd-8th July 2022 VENICE – Live and ONLINE

CEST TIME
(Central European
Summer Time)

SUNDAY 3 July		MONDAY 4 July		TUESDAY 5 July		WEDNESDAY 6 July		THURSDAY 7 July		FRIDAY 8 July	
12:00-17:00	Check-in and Registration at Campus Santa Marta	9:00-10:15	OPENING CEREMONY <i>Janet Scott's Memorial</i>	9:00-9:30	Roman Warhol Organization of Prohibition of Chemical Weapons(OPCW)	9:00-9:15	Eugenia Mescherova PhosAgro-	9:00-9:30	João Borges International Younger Chemists Network (IYCN)	9:00-9:30	Caf Foscari University
		10:15-10:30	Coffee break	10:15-10:30	Pietro Tundo Green Sciences for Sustainable Development Foundation	9:15-9:30	PhosAgro Awards Celebration	10:15-10:30	Buxing Han International Union of Pure and Applied Chemistry (IUPAC)	9:30-10:15	Marco Bella Member of Parliament of Italy
17:00-19:00	WELCOME TOGETHER	10:30-11:30	Krzysztof Matyjaszewski (Jane Wissinger)	9:30-10:00	Buxing Han (Alexei Lapkin)	9:30-10:15	Alessandro Martinis (Christopher Brett)	9:30-10:30	Poster session 7 Exploitation of renewable resources Posters No. 51-62 (Fabio Arico)	10:15-11:00	Carlo Barbante (Jonathan Forman)
		11:30-12:15	Burkhard König (Jane Wissinger)	10:00-10:30	Pietro Tundo (Alexei Lapkin)	10:15-10:45	Vittorio Esposito (Christopher Brett)	10:30-10:45	Coffee break	11:00-11:15	Poster session 10 Climate Change Posters No. 83-92 (Aurelia Visa)
		12:15-13:30	Lunch	10:30-11:00	Haoran Li (Alexei Lapkin)	10:45-11:00	Coffee break	10:45-12:00	Poster Session 8 Exploitation of renewable resources &Health Posters No. 63-77 (Fabio Arico)	11:00-11:15	Coffee Break
		14:00-14:45	Poster Session 1 New reaction pathways Posters No. 1-9 (Aurelia Visa)	11:00-11:15	Coffee break	11:30-12:00	Mirabbos Hojamberdiev (Christopher Brett)	12:00-13:30	Lunch	11:15-12:15	Michael Graetzel (Florent Allais)
		14:45-15:15	Alexei Lapkin (Burkhard König)	11:15-12:15	Jean-Marie Lehn (Krzysztof Matyjaszewski)	12:00-13:00	Oliver Kappe (Christopher Brett)	14:00-14:30	Fabio Arico (Mirabbos Hojamberdiev)	12:15-13:45	Lunch
		15:15-15:45	Jane Wissinger (Burkhard König)	12:15-13:30	Lunch	13:00-14:00	Poster Session 6 Energy saving Posters No. 37-50 (Mirabbos Hojamberdiev)	14:30-15:00	Florent Allais (Mirabbos Hojamberdiev)	14:30-17:00	CLOSING CEREMONY AND POSTER AWARDS
		15:45-16:15	Paul Anastas (Burkhard König)	14:00-14:30	Francesco Trotta (Krzysztof Matyjaszewski)	14:00-16:30	SOCIAL EVENT: BOAT TRIP IN THE VENICE LAGUNE	15:00-15:30	Jonathan Forman (Mirabbos Hojamberdiev)		
		16:15-16:45	Poster Session 2 New reaction pathways Posters No. 10-15 (Aurelia Visa)	14:30-15:00	Martin Möller (Krzysztof Matyjaszewski)	16:30-17:00		15:30-16:00	Coffee break		
		16:45-17:15	Coffee break	15:00-15:30	Aurelia Visa (Krzysztof Matyjaszewski)	17:00-17:30		16:00-16:30	Konstantinos Triantafyllidis (Mirabbos Hojamberdiev)		
		17:15-17:45	Poster Session 3 New reaction Pathways Posters No. 16-21 (Aurelia Visa)	15:30-16:10	Poster session 4 New reaction pathways Posters No. 22-30 (Mirabbos Hojamberdiev)	17:30-18:00		16:30-17:00	Natella Tarasova (Mirabbos Hojamberdiev)		
		17:45-18:45	Poster Evaluation for PhosAgro Award	16:10-16:30	Coffee break	18:00-18:00		17:00-17:30	Emiliano Cazzola (Mirabbos Hojamberdiev)		
				16:30-17:00	Poster session 5 Exploitation of renewable resources Posters No. 31-36 (Mirabbos Hojamberdiev)			17:30-18:00	Poster session 9 Health & Food Safety Posters No. 78-82 (Fabio Arico)		

PROGRAMME

MONDAY, 4 JULY 2022 MORNING

9:00-10.15 OPENING CEREMONY

Presenters:

9:05 – 9:15 **Pietro Tundo** – President of Green Sciences for Sustainable Development Foundation

9:15 – 9:30 **Alessandro Agostinetti** – Regione Veneto: Direttore Direzione Lavoro

9:30 – 9:35 **Tiziana Lippiello** – Ca' Foscari University: Rettrice

9:35 – 9:45 **Paul Anastas** – Director of Yale University's center for Green Chemistry and Green Engineering

9:45 – 9:50 **Buxing Han** – Chair of IUPAC Interdivisional Committee of Green Chemistry for Sustainable Development

9:50 – 9:55 **Siroj Loikov** – Deputy CEO of PhosAgro

9:55 – 10:05 **Ten. Col. Andrea Gloria** – National Authority for the implementation of the Chemical Weapons Convention, Disarmament, Arms Control and Non-proliferation Office, Ministero Affari Esteri, Italy

MEMORIAL JANET SCOTT

10:05 – 10:15 **Natalia Tarasova** – Director of the Institute of Chemistry and Problems of Sustainable Development, Mendeleev University of Chemical Technology of Russia

1st SESSION:

Session Chair: Jane Wissinger

10.30-11:30 **Krzysztof Matyjaszewski**

11:30-12:15 **Burkhard König**

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

12:15-13:30 Lunch

MONDAY 5 JULY AFTERNOON

14:00-14:45 **1st ONLINE POSTER SESSION** “*New Reaction Pathways*” (Poster No. 1-9)

Session Chair: Aurelia Visa

2nd SESSION:

Session Chair: Burkhard König

JULY 3-8, 2022 – ONLINE/IN-PERSON

14:45-15:15 **Alexei Lapkin**
15:15-15:45 **Jane Wissinger**

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

16:15-16:45 **2nd ONLINE POSTER SESSION** *“New Reaction Pathways” (Poster No. 10-15)*

Session Chair: Aurelia Visa

17:15-17:45 **3rd ONLINE POSTER SESSION** *“New Reaction Pathways” (Poster No. 16-21)*

Session Chair: Aurelia Visa

17:45-18:45 In-person Poster Evaluation for PhosAgro Award

TUESDAY, 5 JULY 2022 MORNING

09:00-09:30 **Roman Warchol and Pietro Tundo**

3rd SESSION:

Session Chair: Alexei Lapkin

09:30-10:00 **Buxing Han**

10:00 -10:30 **Pietro Tundo**

10:30-11:00 **Haoran Li**

Session Chair: Krzysztof Matyjaszewski

11:15-12:15 **Jean-Marie Lehn**

TUESDAY, 5 JULY 2022 AFTERNOON

4th SESSION:

Session Chair: Krzysztof Matyjaszewski

14:00-14:30 **Francesco Trotta**

14:30-15:00 **Martin Möller**

15:00-15:30 **Aurelia Visa**

JULY 3-8, 2022 – ONLINE/IN-PERSON

15:30-16:10 4th ONLINE POSTER SESSION *“New Reaction Pathways” (Poster No. 22-30)*

Session Chair: Mirabbos Hojamberdiev

16:30-17:00 5th ONLINE POSTER SESSION *“Exploitation of Renewable Resources” (Poster No. 31-36)*

Session Chair: Mirabbos Hojamberdiev

17:00-18:00 In-Person Poster Evaluation for PhosAgro Award

WEDNESDAY, 6 JULY 2022 MORNING

09:00-09:30 Evgenia Mescherova and Announcement of PhosAgro Award Winners for In-Person Poster Presentations

5th SESSION:

Session Chair: Christopher Brett

09:30-10:15 Alessandro Martinis

10:15-10:45 Vittorio Esposito

11:00-11:30 Mirabbos Hojamberdiev

11:30-12:00 Oliver Kappe

12:00-13:00 6th ONLINE POSTER SESSION *“Energy Saving” (Poster No. 37-50)*

Session Chair: Mirabbos Hojamberdiev

14:00-20:00 Social event

THURSDAY, 7 JULY 2022 MORNING

09:00-09:30 João Borges and Buxing Han

09:30-10:30 7th ONLINE POSTER SESSION *“Exploitation of Renewable Resources” (Poster No. 51-62)*

Session Chair: Fabio Aricò

JULY 3-8, 2022 – ONLINE/IN-PERSON

10:45-12:00 8th ONLINE POSTER SESSION *“Exploitation of Renewable Resources and Health”*
(Poster No. 63-77)

Session Chair: Fabio Aricò

THURSDAY, 7 JULY 2022 AFTERNOON

6th SESSION:

Session Chair: Francesco Trotta

14:00-14:30 **Fabio Aricò**

14:30-15:00 **Florent Allais**

15:00-15:30 **Jonathan Forman**

16:00-16:30 **Konstantinos Triantafyllidis**

16:30-17:00 **Natalia Tarasova**

17:00-17:30 **Emiliano Cazzola**

17:30-18:00 9th ONLINE POSTER SESSION *“Health and Food Safety”* (Poster No. 78-82)

Session Chair: Fabio Aricò

FRIDAY, 8 JULY 2022 MORNING

09:00-09:30 **Marco Bella**

7th SESSION:

Session Chair: Jonathan Forman

09:30-10:15 **Carlo Barbante**

10:15-11:00 10th ONLINE POSTER SESSION *“Climate Change”* (Poster No. 83-92)

Session Chair: Aurelia Visa

8th SESSION:

Session Chair: Florent Allais

JULY 3-8, 2022 – ONLINE/IN-PERSON

11:15-12:15 Michal Graetzel

FRIDAY, 8 JULY 2022 AFTERNOON

14:30-17:00 Announcement of Online Poster Award Winners and Closing Ceremony

Group Photo

JULY 3-8, 2022 – ONLINE/IN-PERSON

SUMMER SCHOOL TOPICS

1. New reaction pathways
2. Exploitation of renewable resources
3. Energy saving
4. Health
5. Food safety
6. Climate change

ABSTRACTS OF PLENARY LECTURES

JULY 3-8, 2022 – ONLINE/IN-PERSON

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 reversibly, 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 *evolutionary chemistry*.

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REACTION MECHANISM AND GIBBS 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 new reaction pathways in syntheses; they, if coupled with metrics measurement, are the scientific and fundamental bases of green chemistry, provided that they have a higher selectivity and occur with lower energy profile. Due to its benign nature, Dimethyl Carbonate (DMC) 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. Many ambident nucleophiles are known, but ambident electrophiles are only a few. Organic Carbonates are ambident electrophiles and follow exemplarily the Pearson's HSAB theory, so resulting in reactions with a unprecedented selectivity. The activation energy of the S_N2 reaction pathway is further decreased by entropic factors if formation of cycles is involved.

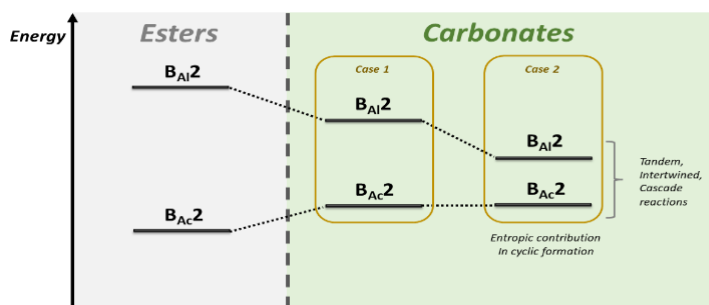


Figure. Activation energies in Esters and Carbonates; only B_{Ac2} and B_{Al2} reaction mechanisms are shown. Ingold's terminology is adopted for esters and carbonates.

The comparison among Esters and Carbonates concerning different reaction mechanisms will be shown (Figure). The nucleophilic attack proceeds differently in Esters and Carbonates. In methyl acetate the reactions take place on the sp^2 carbonyl moiety; in dimethyl carbonate the nucleophilic attack to the sp^3 carbon is much easier. Moreover, the reagent is modified during the reaction, so different reactions can take place in sequence in the same pot: tandem reaction, cascade, and intertwined reactions are possible in carbonates. S_N2 Nucleophilic substitution reactions at saturated and acyclic 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. Reporting on the relationship among Carbonates and Esters will give an easier speculation on a chemistry not yet satisfactorily explored from a fundamental view and will make possible the development of a Model for understanding the factors that control activation barriers and an exploitation of a chemistry beyond chlorine, as well.

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JULY 3-8, 2022 – ONLINE/IN-PERSON

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.

JULY 3-8, 2022 – ONLINE/IN-PERSON

ALESSANDRO MARTINIS

Vice President

Danieli Centro Metallics

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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.

JULY 3-8, 2022 – ONLINE/IN-PERSON

CARLO BARBANTE

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**TOO LATE FOR 2°C? FROM THE PARIS AGREEMENT TO THE CLIMATE OF
TOMORROW**

JULY 3-8, 2022 – ONLINE/IN-PERSON

KRZYSZTOF MATYJASZEWSKI

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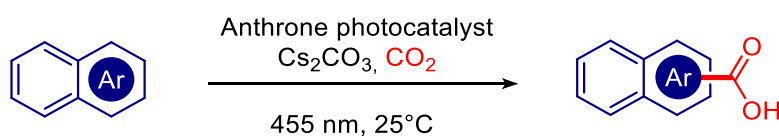
GREEN MATERIALS BY ATOM TRANSFER RADICAL POLYMERIZATION UNDER BENIGN CONDITIONS

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.

USING VISIBLE LIGHT FOR MORE SUSTAINABLE ORGANIC SYNTHESIS

Ideal chemical transformations in terms of green and sustainable chemistry convert abundant, low energy starting materials into high value products without losing a single atom.¹ Light-driven catalysis offers tools for such reactions.² We discuss in the lecture key photocatalytic principles and how they can be applied to redox-neutral reactions, such as C-H carboxylations of alkanes and arenes with carbon dioxide.³ Current scope and limitations are shown and a perspective is provide where the use of light may lead to better catalysis.



Redox-neutral photocatalytic C-H carboxylation

Acknowledgement



¹ Trost, B.M., *Science* **1991**, 254, 1471 – 1477.

² Marzo, L.; Pagire, S.K.; Reiser, O.; König, B. *Angew. Chem. Int. Ed.* **2018**, 57, 10034 – 10072.

³ Donabauer, K.; König, B. *Acc. Chem. Res.* **2021**, 54, 242–252.

ABSTRACTS OF LECTURES

JULY 3-8, 2022 – ONLINE/IN-PERSON

FLORENT ALLAIS

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

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

Located in the CEBB (European Center of Biotechnology and Bioeconomy, co-funded by the ERDF, the Grand Est Region, the Marne department and the Urban Community of Grand Reims) at the heart of the Pomacle-Bazancourt biorefinery, the URD ABI is interested in the valorization of biomass.

Thanks to its expertise in chemistry, polymers/materials, microbiology/biochemistry/molecular biology, chemical engineering and separation process engineering as well as in analytical chemistry, the URD ABI is able to carry out multi- and transdisciplinary fundamental and applied research projects with the ambition of developing and optimizing sustainable industrial processes and high value-added products from agro-resources and industrial by-products.

This talk will provide some illustrative examples on how lignocellulosic biomass can be efficiently transformed into flavors, antioxidants, UV filters, monomers, polymers etc... by combining biotechnologies, green chemistry and process engineering.

JULY 3-8, 2022 – ONLINE/IN-PERSON

PAUL T. ANASTAS

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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.

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].

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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.

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JULY 3-8, 2022 – ONLINE/IN-PERSON

VITTORIO ESPOSITO

ARPA Puglia, Environment Agency of Apulia, Italy

**COMMAND-AND-CONTROL VS POLLUTION PREVENTION IN
ENVIRONMENTAL POLICIES FOR ACHIEVING GREEN AND
SUSTAINABLE STEEL PRODUCTION IN ITALY**

Integrated pollution control is an important part of the move towards a more sustainable balance between human activity and socioeconomic development, whereas action is required at the global level in order to modify and supplement existing legislation concerning the prevention and control of pollution from industrial plants. The role of governments and public authorities is presented in this lecture, with particular reference to the metal sector. The Environment Protection Agency of Apulia has performed several measurements of Persistent Organic Pollutants (POPs) emissions for a number of industrial plants located in a large industrial area near Taranto, Italy, where stack, diffuse and fugitive emissions are contributing to the overall impact on the surroundings resulting in a measurable POPs atmospheric deposition of both wet and dry matter on soils and other urban surfaces. Although estimates of a significant yearly mass flow for dioxins from industrial sources and especially for the local integrated steelwork were already available and published in relevant European inventories since the year 2000, the actual measurements were in exceedance of those estimates and prompted the need of a more in-depth investigation of the fate and transport of POPs from emissions and release to the various environmental compartments and ultimately to transfer to the food-chain. An introduction to the principles of sustainable steelmaking is also presented.

JULY 3-8, 2022 – ONLINE/IN-PERSON

JONATHAN E. FORMAN

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**CHEMICALS OF WAR AND PEACE:
ARMS CONTROL, DISARMAMENT, NON-PROLIFERATION, AND GREEN
CHEMISTRY?**

Harmful properties of chemicals have been exploited for weaponization throughout the history of warfare, likewise there is also a history of efforts to limit, control, and/or completely ban certain chemicals from being used in war. Within the various arms control, disarmament, and non-proliferations agreements, chemistry intersects with legal obligations and diplomatic efforts. This lecture will discuss chemicals of war and the international agreements that seek to prevent their use in warfare. The discussion will look at where policy considerations and chemistry both challenge and support one another. and how the descriptions of chemicals within the agreements influence the processes and policies of treaty implementation. While green chemistry seeks to discover “less hazardous” chemicals, it must also be appreciated that it is the dose that makes the poison, which begs the question “can green chemistry be used in warfare, and what implications does this have for how we practice green chemistry?”. Similarly, if a chemical is designed to be “less harmful”, and developed for peaceful and benign purposes, does this reduce or remove the risk that such a chemical might be used maliciously by those with harmful intent? For the Green Chemistry Postgraduate Summer School, students will be asked to consider these questions and look at how green chemistry relates to the broader objectives of chemical security.

BUXING HAN

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CONVERSION OF CO₂ AND BIOMASS INTO CHEMICALS AND FUELS

Carbon dioxide (CO₂) is the main greenhouse gas, and it is also a renewable, abundant, and cheap C₁ feedstock. Biomass is abundant renewable carbon resource. Use of CO₂ and biomass as carbon source to produce fuels and value-added chemicals is of great importance for the sustainable development of our society and achieving the goal carbon neutrality. In recent years, we are very interested in catalytic conversion CO₂ and biomass. In this presentation, I would like to discuss some of the recent results in our group on design of green solvents, green catalysts and their application in conversion of CO₂ and biomass into valuable chemicals and fuels [1-18].

Acknowledgements

The speaker thanks the National Key Research and Development Program of China (2017YFA0403103), National Natural Science Foundation of China (21733011, 21890761, 22121002), the Chinese Academy of Sciences (QYZDY-SSW-SLH013) for the financial support.

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PEROVSKITE BaTaO₂N FOR GREEN HYDROGEN GENERATION FROM SOLAR WATER SPLITTING

Although hydrogen is a zero-emission energy carrier, its current global production still heavily relies on fossil fuels. Current momentum on renewable energy and environmental remediation is unprecedented because of fast climate change. We all know that the world is hurrying up to achieve the United Nations Sustainable Development Goals (SDGs) by 2030 without pausing even during the COVID-19 pandemic. One of the important SDGs is Goal 7: Affordable and Clean Energy. As a replica of natural photosynthesis, a semiconductor-based artificial photosynthetic system is regarded as one of the most economically viable, highly efficient, and environmentally benign chemical processes to generate green hydrogen energy from solar water splitting. However, to harness solar energy efficiently, it is necessary to enhance the visible-light-driven photocatalytic performance of the existing materials and to discover novel visible-light-active materials. Mixed-anion compounds offer new opportunities in this regard. As a 600 nm-class photocatalyst, BaTaO₂N has received particular attention due to its small bandgap ($E_g = 1.8$ eV), suitable band edge positions for visible-light-induced water splitting, chemical stability, and nontoxicity. BaTaO₂N is routinely synthesized by a two-step method: (i) the synthesis of a corresponding oxide precursor and (ii) its high-temperature nitridation under an NH₃ atmosphere for a prolonged period. This two-step method leads to the formation of various defects that negatively affect the water splitting performance.

Therefore, we have (i) applied an NH₃-assisted direct flux growth approach to reduce the defect density of BaTaO₂N, (ii) engineered the bandgap by cation substitution, and (iii) explored the effects of the altered morphology, size, and porosity on the visible-light-induced water oxidation activity and photoelectrochemical performance of BaTaO₂N. The findings revealed that the photocatalytic activity and photoelectrochemical performance of BaTaO₂N were significantly influenced by its morphology, size, porosity, substituent type, and substitution concentration. Particularly, the BaTaO₂N crystal structures obtained by nitridation of oxide precursor without KCl flux exhibited a higher surface area and high anodic photocurrents compared to the BaTaO₂N crystal structures obtained by nitridation of oxide precursor with KCl flux due to the high number of dangling bonds acted as a nucleation centers for the highly dispersed CoO_x cocatalyst nanoparticles. Also, an NH₃-assisted direct flux growth approach reduced the density of intrinsic defects in BaTaO₂N crystals, leading to the substantial enhancement in water oxidation activity. The Mg-substituted BaTaO₂N and Al-substituted BaTaO₂N independently exhibited the highest amounts (in 5 h) of evolved O₂ (503.6 μ mol) and H₂ (117.4 μ mol), respectively, whereas the Zr-substituted BaTaO₂N showed the high photocatalytic activities in both O₂ (446.8 μ mol) and H₂ (80.4 μ mol) half-reactions due to the altered potentials of the valence and conduction bands and an increased density of charge carriers.

Acknowledgements: This project received funding from the European Union's Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie grant agreement no. 793882.

GOING WITH THE FLOW – THE USE OF CONTINUOUS PROCESSING IN ORGANIC SYNTHESIS

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).

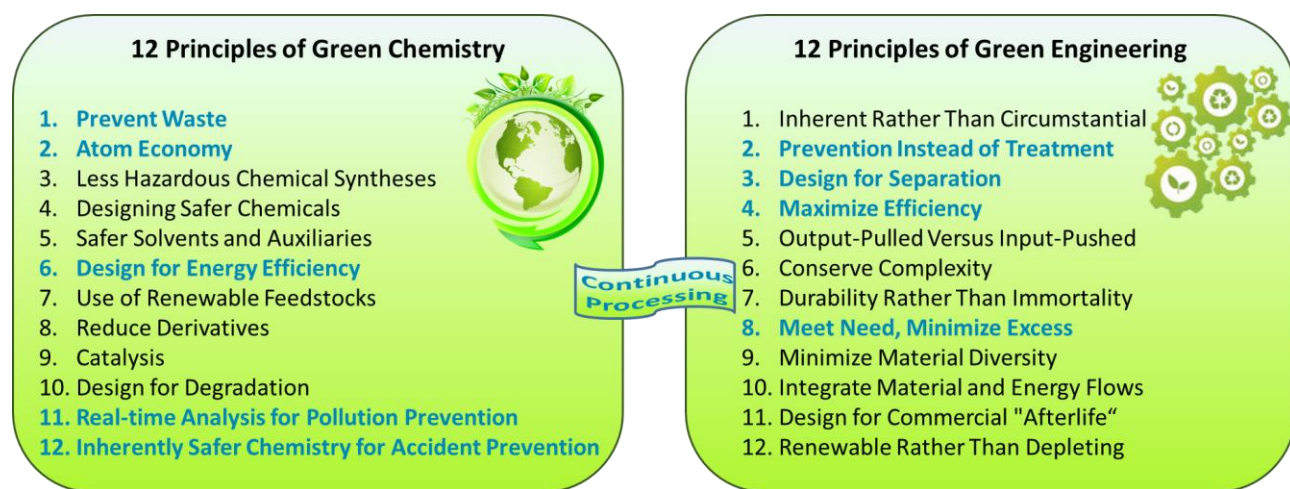


Figure 1. Twelve principles of green chemistry and green engineering and the impact of continuous processing highlighted in blue [2].

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JULY 3-8, 2022 – ONLINE/IN-PERSON

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ARTIFICIAL INTELLIGENCE TOOLS FOR DEVELOPING GREENER CHEMICAL SOLUTIONS

One of key problems in developing green chemistry solutions is the understanding of multiple interactions that may affect the ‘greenness’ (e.g., a ‘green solvent’ resulting in significant increase in energy intensity of a process, and more complex interactions). To reveal such interactions, it is necessary to analyse interactions as a network. This is facilitated by the ongoing digitalisation of chemical R&D. Access to digitised data about molecules, reactions and process, as well as new ML-accelerated computational tools allow to assemble the required research tasks and use algorithmic research methods to analyse large amounts of data from literature as well as from high-throughput automated experiments. In this lecture we’ll look at the fundamentals of digital chemical development workflow and examples of applications to tasks such as solvent substitution and reduction of environmental impact of chemical transformations.

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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.

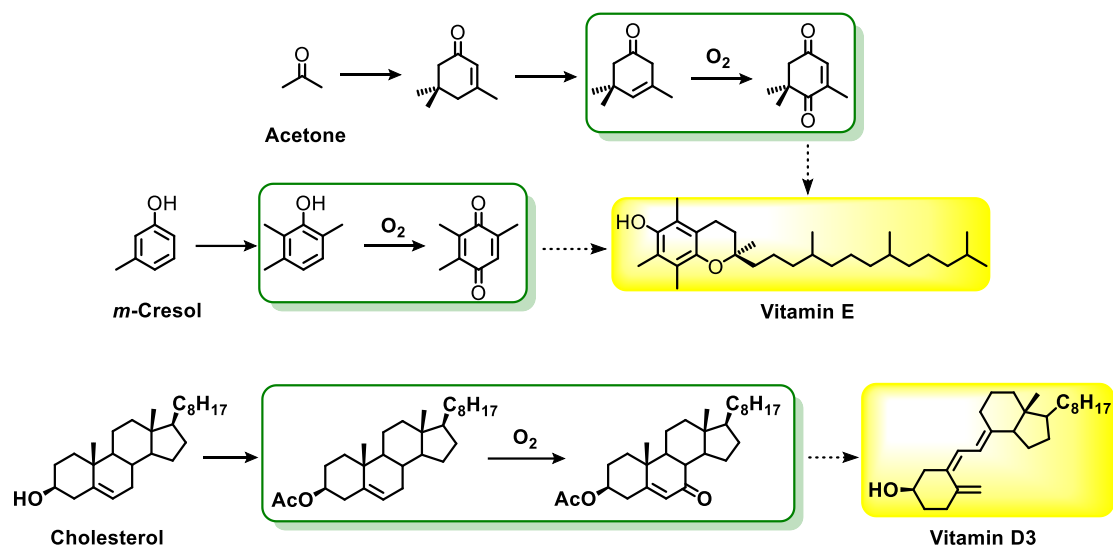


Figure 1. The brief industrial routes for production of vitamin E and vitamin D3.

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THE INNOVATION POTENTIAL OF BIOINSPIRED MATERIALS

Living organisms synthesize materials with often surprising functions and adaptation capabilities and are at the same time they are part of a natural circular economy. In order to achieve this, Nature uses a small number of building blocks which are assembled in often extremely complex structures. Structural complexity does not only enable very specific combinations of properties which are at the first glance conflicting like soft and strong, but provides also means to program adaptability and active response. This is where the inspiration from nature comes in: structural complexity and diversity, constantly adapting structures and the resulting functional characteristics show new ways to design, synthesize and process materials, which ultimately to encompass all structural levels from the molecule to the the device. It is already clear from many examples that bioinspired materials design or “biologicalization of material Science will have a major contribution to reorientation of materials research from established structure-property relations correlations towards programming functionality and adaptability. This reorientation involves many future fields, such as lightweight constructing, medicine, robotics, or energy harvesting.

For the biologization of materials Science, we identify four major criteria: (i) cross scale synthesis technologies as a prerequisite for (ii) a information content of the material structure and extended functionality, (iii) the possibility to select smart structure, which have the “right” properties and (iv) the use of complex natural building block and natural processes.

Cross Scale Synthesis

Future developments depend on rapid further development of our capabilities to synthesize ever more complex structures. This entails widening our understanding of synthesis to encompass substantially more than “merely” the formation of chemical bonds and production of molecules. Synthesis will increasingly require complete mastery of structure and the creation of properties across all length scales. This includes the entire chain from atom to molecule to nanoscopic building blocks to their combination on the micrometre scale right up to a component's macroscopic structural elements. Today, the pathway from molecule to component is broken down into very clear individual development stages, with experts for each length scale who develop their methods and specialist knowledge in dedicated disciplines before passing on and combining the outcome of their work. In contrast, Nature's growth processes offer a fully integrated synthesis technology which permits the construction of complex hierarchical structures with particular and active properties from comparatively few basic building blocks.

High Information Content of material.

In biological materials, the information about their functional properties, for example for sensing, actuation or signal generation, is stored in the internal structure. Also within synthetic materials the hierarchically organized structure of synthetic materials, molecules, superstructures, complexation and switchability between different states can encode information for responsive and adaptive properties. However, the complexity and diversity of structures also gives rise to another aspect of the “biologicalization of materials science”, namely the necessity of programming the particular “smart” functions, which corresponds to the selection of the right structures

Selection of the “right” structures.

By Nature, selection has been accomplished during evolution and each function has been programmed by a huge number of trial and error steps. While increasing use may indeed be made of evolutionary selection principles, associated with high-throughput methods for keeping their time requirements within bounds, accelerated technical development can only succeed if we have a good understanding of the complex interactions. The synthesis and production of new complex material structures, making use of specific interactions, can only succeed with the assistance of new theoretical

models and numerical simulations which make it possible to capture all the interrelationships at different scales of length and time. Yet, complex mathematical models and simulations are increasingly the only way to interpret and evaluate the profusion of data. Non-destructive and, in particular, real-time characterization, in conjunction with real-time data evaluation throughout a product's production process and service life, are becoming ever more significant for materials technology and processing.

Natural Components and Processes.

In addition to these three aspects of the "biologicalization of materials science" outlined above, which present a challenge far beyond the use of biological components, there are also increasing calls to give primacy to natural components. This fourth aspect follows from the urgent necessity for new synthesis and use technologies which are compatible with or can be integrated into natural cycles. Besides moving away from petroleum-based primary materials and reducing environmental impact, we can take enormous advantage by using natural production processes and employing natural preproducts which come with an advanced structural complexity and functionality. This requires water-based, non-toxic chemical processes and mastery of physical transformations and self-assembly processes. Established examples are water-based coating materials and coatings, adhesives and also applications in the construction and cosmetics sectors.

If the above four criteria are summed up, it becomes clear that we are today "at a tipping point in science and engineering", i.e. at the start of a challenging new development which contains elements of a paradigm shift.² Only if there is close cooperation between macromolecular chemistry, polymer technology, polymer physics and mathematical simulation will it be possible to expect new and progressive responses for stabilization, predictability, self-healing and also controlled ageing. Taking molecular materials by way of example, Figure 1 addresses the technological and scientific prerequisites with which these challenges can be successfully met in future so that the "biologicalization of materials science" as an emerging field of research can take on great practical significance.

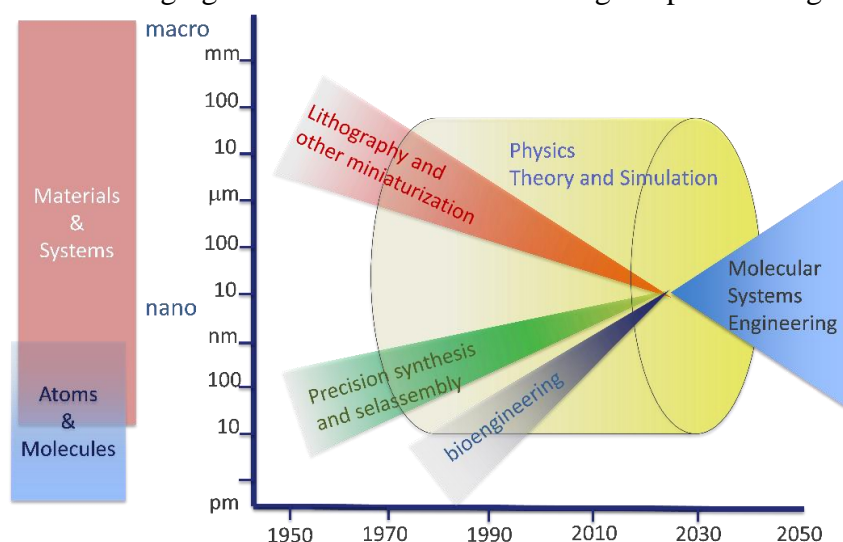


Figure 1: Drivers and interdisciplinary links for the development of complex molecular materials. In addition to mastering ever smaller length scales in lithographic and additive processes (top-down), progress is determined by an increasing ability to synthesize and perform molecular simulations of ever larger units (bottom-up) (source: Martin Möller, Leibniz Institute for Interactive Materials).

Besides discussing these general aspects of the Biologicalization of Materials Science, I will present two selected examples of such advanced material concepts, the first is a light propelled microswimmer, the second one are synthetic vesicles that can engulf particles and bacteria.

² | As was stated when the Wyss Institute at Harvard University was founded in 2009: "...we are now at a tipping point in the history of science and engineering – we are beginning to understand enough about how Nature builds, controls and manufactures that entirely new engineering principles are already beginning to be discovered".

NATALIA TARASOVA

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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].

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ADDING VALUE TO BIOREFINERY AND PULP INDUSTRY SIDE-STREAMS: LIGNIN VALORIZATION TO FUELS, CHEMICALS AND POLYMERS

Lignin is the most abundant natural aromatic/phenolic polymer and is one of the main structural components of lignocellulosic biomass, the other two being hemicellulose and cellulose. It is widely available in > 1 Mton annually in the form of lignosulphonate (mainly), kraft and soda sulphur-free lignins, as by-product of the pulp and paper industry. In the last twenty years, the intensive efforts of converting biomass to high added value fuels, chemicals and materials via the so-called “biorefinery” processes, such as the production of 2nd generation (cellulosic) bioethanol, has also led to the recovery of lignin streams, either as the remaining of acid/enzymatic hydrolysis of biomass carbohydrates or as initially isolated fraction via the organosolv and related “lignin-first” approaches. Despite the high potential of lignin as a low cost (waste / side-product) raw material for the liquid fuel and chemical industry, it is still under-utilized compared to the carbohydrate fractions of biomass, being mainly burnt to cover the heat and power needs of the main process, i.e. pulping, hydrolysis.

In this presentation, we will discuss the state of the art, as well as recent results of our group, on lignin production (biomass fractionation), characterization and valorization processes that are currently being developed and exhibit high exploitation potential. With regard to the down-stream processing, emphasis is placed on fast pyrolysis and hydrogenolysis of lignin which are capable to provide bio-oils that contain valuable phenolic and/or aromatic (BTX) compounds [1-5]. Such bio-oils can be hydrodeoxygenated (HDO) towards hydrocarbon fuels or can serve as source of monomers for the production of phenolic or epoxy resins or BTX based polymers. Due to the intrinsic functionality of lignin (surface hydroxyls) and its high aromaticity, it can also be utilized as reactive additive in epoxy or phenolic resins, without previous depolymerization to its monomer phenolic building units, thus reducing the need for petroleum-based monomers. However, appropriate functionalization can offer additional benefits towards bio/lignin-based polymers and composites.

Acknowledgements

The support by the project “INVALOR: Research Infrastructure for Waste Valorization and Sustainable Management” (MIS 5002495) which is implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greek National Funds and the European Union (European Regional Development Fund) is gratefully acknowledged. The authors would also like to thank Prof. P. Christakopoulos (Lulea University of Technology) for providing various samples of spruce and birch derived lignins for characterization and pyrolysis experiments. The contribution of COST Action LignoCOST (CA17128), supported by COST (European Cooperation in Science and Technology), in promoting interaction, exchange of knowledge and collaborations in the field of lignin valorization is gratefully acknowledged.

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JULY 3-8, 2022 – ONLINE/IN-PERSON

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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 eco-friendly 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 dextrans 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.

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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.

Acknowledgement

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JULY 3-8, 2022 – ONLINE/IN-PERSON

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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.

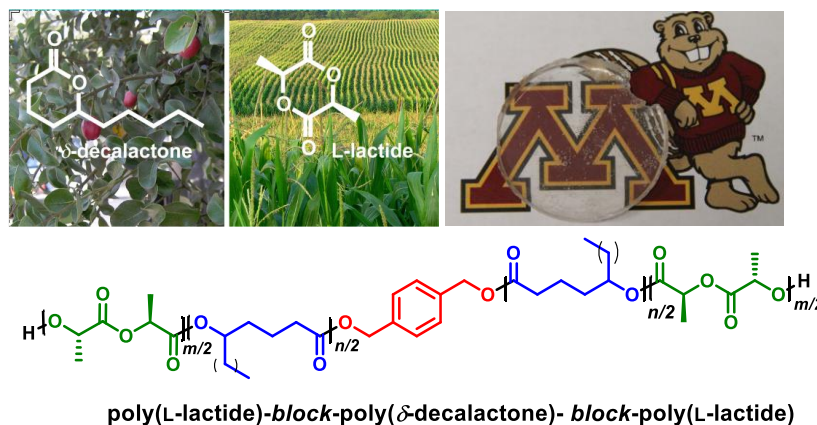


Figure 1. Sustainable Polymer Teaching Lab Experiment

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ABSTRACTS OF STUDENTS

The abstracts are divided by the topics of the Summer School:

- 1. New reaction pathways**
- 2. Exploitation of renewable resources**
- 3. Energy saving**
- 4. Health**
- 5. Food safety**
- 6. Climate change**

Legends:

- ★ Only abstract**
- ★★ Abstract and Poster**
- ★★★ Abstract and Poster presented in one of the Poster Sessions**
- ★★★★ Abstract and Poster presented during one of the Poster Sessions and awarded in Closing Ceremony**

1. NEW RESEARCH PATHWAYS

POSTER No. 1

Asymmetric poly(ionic liquid)–ionic liquid membranes for gas separation

Bruna F. SOARES, Isabel M. MARRUCHO

POSTER No. 2

A multi-gram synthesis to pure HMF and BHMF

Beatriz CHÍCHARO, Giovanna MAZZI, Giacomo TRAPASSO, Mattia ANNATELLI, Davide DALLA TORRE, Fabio ARICÒ

POSTER No. 3

Thermal reactions of cyclohexen-1,3-oxazine and 1,3-thiazine cis-fused cyclohexen-1,3-oxazines studied from green metrics

Diana C. PINILLA PEÑA, Zsolt SZAKONYI and Walter J. PELÁEZ

POSTER No. 4

A Further Step to Sustainable Hydroformylation

Fábio G. DELOLO, Ji YANG, Helfried NEUMANN, Eduardo N. dos SANTOS, Elena V. GUSEVSKAYA, Matthias BELLER

POSTER No. 5

Metal phosphide nanoparticles for the hydrotreatment of methyl laurate to produce green liquid fuels

Diana GARCÍA-PÉREZ, M. CONSUELO ÁLVAREZ-GALVÁN, M.C. CAPEL-SÁNCHEZ, José M. CAMPOS-MARTÍN, Susan HABAS

POSTER No. 6

Reactivity of Ruthenium Acetylide Complexes Towards Carbon Dioxide

Silviu DOBROTA, Hsiu L. LI, and Leslie D. FIELD

POSTER No. 7

Exploring Mechanisms in Iodine Catalysis

Domenic PACE and Vinh NGUYEN

POSTER No. 8

Sustainable Gold Extraction via Host-Guest Chemistry

Lucy L. FILLBROOK, Pall THORDARSON, J. Fraser STODDART, Jonathon E. BEVES

POSTER No. 9

Research on the preparation of mono-benzene aromatic compounds by catalytic hydrogenolysis of lignin

Jian WEI, Weize WU

POSTER No. 10

Design, Synthesis and Characterization of Iridium(III), Ruthenium(II) and Palladium(II) Complexes and their Evaluation in the Hydrodeoxygenation of (E)-6-(furan-2-yl)-4-oxohex-5-enoic acid

Gracious KAUNDA, Banothile MAKHUBELA, Leah MATSINHA

POSTER No. 11

Catalytic hydrosilylation of alkynes and imines in green solvents

Mostafa KREIK, Kinga STEFANOWSKA, Adrian FRANCZYK, Jakub SZYLING, Tomasz SOKOLNICKI, Jędrzej WALKOWIAK

POSTER No. 12

Green oxidation of phenols and naphthols on silica-supported gold and ruthenium catalysts

Tumisang LEKGETHO, Mabuatsela MAPHORU, Letlhogonolo MABENA, Matshawandile TUKULULA

POSTER No. 13

Eco-friendly Uracil Selenylation Employing I₂/DMSO as a Catalytic Oxidation System

Maria Eduarda THEDY, Juliano Braun AZEREDO, Antonio Luiz BRAGA

POSTER No. 14

Selective Cu and Ni-MOFs as pre-catalysts for the hydrogenation of furfural to furfuryl alcohol

Pamela. S. MOYO, Leah. C. MATSINHA, Banothile. C.E. MAKHUBELA

POSTER No. 15

La(III) Schiff Base Complexes: Microwave-Assisted Synthesis, Physicochemical and Spectroscopic Analysis

Nur Husnina NASARUDDIN, Shahrul Nizam AHMAD, Hadariah BAHRON, Nor Mas Mira ABD RAHMAN and Nor Saadah Mohd YUSOF

POSTER No. 16

Ethanol as a Green Solvent for the Catalytic Applications of a Heterobimetallic Compound in Tandem Transformations

Mahshid NIKRAVESH and Hamid R. SHAHSAVARI

POSTER No. 17

The versatility of Acetamido-TEMPO in the chemical and electrochemical activated oxidation of alcohols

Fabrizio POLITANO, William P. BRYDON, Chelsea SCHROEDER, Arturo LEON SANDOVAL, Nicholas E. LEADBEATER

POSTER No. 18

Green synthesis of glycerol-derived surfactants for environmental applications

Prisco PRETE, Tommaso TABANELLI, Filippo BRUNO, Antonio PROTO, Raffaele CUCCINIELLO

POSTER No. 19

Multicomponent reactions as a green strategy for syntheses of complex molecules

Seyyed EMAD HOOSHMAND

POSTER No. 20

Conversion of CO₂ to value-added products through a CuZnO-Cu/Zeolite ZSM-5 hybrid catalyst

Dalia SANTA CRUZ-NAVARRO, Miguel TORRES-RODRÍGUEZ, Violeta MUGICA-ÁLVAREZ, Sibeles PERGHER

POSTER No. 21

Microwave-assisted synthesis of non-noble metal nanoparticles for plasmonic applications

Arti SHARMA, Jatin, Tripti AHUJA, Soumik SIDDHANTA

POSTER No. 22

Stereoselective synthesis of functionalized pyrrolidines from aldehydes

Nkwane THOBEJANE and Comfort NKAMBULE

POSTER No. 23

Structural diversification of diterpenes through complementary peroxidic oxidations

Maria Luz TIBALDI BOLLATI, Gonzalo GUENDULAIN, Fabricio Román BISOGNO, Manuela Emilia GARCIA

POSTER No. 24

Oxidation of aminophenols on Ru-Au and Ru-Pd nanocatalysts supported on titanium oxide

T.P. MNTAMBO, M.V. MAPHORU, L.F. MABENA, M. SHOZI

POSTER No. 25

Preparation of industrial primary alcohols by a one-pot hydroboration-isomerization process from waste polyolefin pyrolysis oil

Trang THI BUI, Sven JANSSENS, Lukasz PAZDUR, Christophe VANDE VELDE, Pieter BILLEN, Serge M.F. TAVERNIER

POSTER No. 26

Large scale synthesis of dialkyl carbonates and their application as green solvents for PVDF membranes preparation

Giacomo TRAPASSO, C. SALARIS, M. REICH, E. LOGUNOVA, C. SALATA, K. KÜMMERER, F. GALIANO, F. RUSSO, C.R. MCELROY, J. SHERWOOD, A. FIGOLI, F. ARICÒ

POSTER No. 27

Green Synthesis of an Eggshell-Derived Calcium-Terephthalate Metal-Organic Framework

Gizelle VAN NIEKERK and Henrietta LANGMI

POSTER No. 28

Study of the Synergic Interactions of Ascorbic and Dihydroxyfumaric Acids by EPR Spectroscopy

Crina VICOL, Alexandra IACOBESCU, Adrian FIFERE, Gheorghe DUCA

POSTER No. 29

Synthesis and investigation of new polycyclic *n*-heterocycle compounds via multicomponent reactions from 3-alkoxy-1*H*-pyrazole-4-carbaldehydes

Viktorija Dargytė, Eglė Arbačiauskienė, Aurimas Bieliauskas, Algirdas Šačkus

POSTER No. 30

Highly efficient separation of benzene + cyclohexane mixtures by extraction combined extractive distillation using imidazolium-based dicationic ionic liquids

Wanxiang Zhang and Weize Wu

2. EXPLOITATION OF RENEWABLE RESOURCES

POSTER No. 31

Composite systems for photoelectrochemical reduction of CO₂

Aleksandra Parzuch

POSTER No. 32

5,5'(Oxy-bis(methylene)bis-2-furfural (OBMF) from 5-hydroxymethyl-2-furfural (HMF): a systematic study for the synthesis of a new platform molecule from renewable substances

Mattia ANNATELLI, Giovanna MAZZI, Fabio ARICO

POSTER No. 33

Sustainable Terahertz (THz) Electromagnetic Shields Based on Conductive Biochar-Nanocellulose Composites

Avinash R Pai, Sabu Thomas

POSTER No. 34

Saponins from the rind of *Napoleonaea imperialis* P. BEAUV

Gloria NDUKWE, Rachael EKONG and Ibiba JACK

POSTER No. 35

Microalgae *Chlamydomonas reinhardtii* extracts and their antimicrobial activity

Elia Lio, Giancarlo Aldini, Francesco Secundo

POSTER No. 36

Single-step production of green butadiene over bimetallic silica-supported catalysts

Silmara FURTADO DA SILVA, Luiza Cardoso CINTRA, Maria Letícia MURTA VALLE

POSTER No. 51

Preparation of nanobiocomposites based on halloysite nanotubes-zein and evaluation of their performance for thin film microextraction

Hasti GORDAN, Vahideh MAHDAVI, Arnavaz Keikavousi BEHBAHAN, Habib BAGHERI

POSTER No. 52

New insights into CO₂ suppression in biomass oxidation to formic acid catalyzed by vanadium-substituted heteropolyacids

He Zhuosen and Wu Weize

POSTER No. 53

Study of the Functional Groups Associated with the Corrosion Inhibition of Stainless Steel Arch Bar in Acidic Medium by Khaya Grandifolia Gum Exudate

Naziru Imam, K.I. Omoniyi and P.O. Ameh

POSTER No. 54

Preatreatment of seawater by ceramic membranes prepared by alternatives raw materials

Fatma KESRI, Djilali TASSALIT, Zahia TIGRINE and Nadia Aicha LAOUFI

POSTER No. 55

Biodiesel production using cellulose-supported calcium hydroxide heterogeneous catalyst synthesized from phosphate rock

Janet KIPRONO, Hilary RUTTO, and Tumisang SEODIGENG

POSTER No. 56

The HMF, the key to green chemistry through the circular economy

Marta LARA-SERRANO, Daniela M. SBOIU, Silvia MORALES-delaROSA, Jose Miguel CAMPOS-MARTIN

POSTER No. 57

Comparative study of three eco-friendly green materials for inhibition and control of mild steel corrosion

Anthony OBIKE and Emmanuel OGILI

POSTER No. 58

Health risk assessment of trace metals in vegetables and soil within the vicinity of First Technical University, Ibadan, Oyo State

Dorcas Abosede OKE and Ayodeji Jacob OGUNSANYA

POSTER No. 59

Isolation and Characterization of Starch from *Citrus sinensis* Albedo as Bioplastics

Jacob Sunday OYEKU and Samson Olugbemiga ALAYANDE

POSTER No. 60

Fatty acid conversion to value-added chemicals and fuel additives by La-promoted Ni/SBA-15 catalyst

Sibongile PIKOLI and Banothile C.E. MAKHUBELA

POSTER No. 61

Bioplastics that grow on trees

Daniela M. SBOIU, Marta LARA-SERRANO, Silvia Morales-delaROSA, Jose M. CAMPOS MARTÍN

POSTER No. 62

New bio-based sustainable polymers and polymer composites based on methacrylate derivatives of furfural, solketal and lactic acid.

Raynold TECHIE-MENSON, Charles K. RONO, Anita ETALE, Gift MEHLANA, James DARKWA, and Banothile C.E. MAKHUBELA

POSTER No. 63

Characterization of food waste and sugar wastewater for biogas production

Zikhona TSHEMESE, Nirmala DEENADAYALU, Linda LINGANISO, and Maggie CHETTY

POSTER No. 64

Performance Evaluation of Glutaraldehyde-Modified Polyphenolic Resin as Oilfield Scale Inhibitors

Dominica UNA, Cynthia VICTOR-OJI, Dulu APPAH, Amieibibama JOSEPH, and Onyewuchi AKARANTA

POSTER No. 65

Conversion of hemicellulosic biomass into furan derivatives

Winifred D. ANYOMIH and Banothile, C.E. MAKHUBELA

POSTER No. 66

Formulation and Characterization of the Natural Fiber/Polymer Composites from Waste Pineapple Leaf Fibers

Zikhona TYWABI-NGEVA and Mohau PHIRI

3. ENERGY SAVING

POSTER No. 37

Photocatalytic activity of ZnO and Al-ZnO nanocatalysts for organic dye degradation under UV irradiation

Myriam CHEMS, Kaoutar EL HASSANI, Hajar JABKHIRO and Abdellah ANOUAR

POSTER No. 38

Betacyanin geometrical isomers and their conformers with selected organic sensitizer (L0) in forming complexes dye towards dye sensitized solar cell application

Rene COSTA, Ohoud S. AL-QURASHI and Nuha WAZZAN

POSTER No. 39

Development of a flow platform for the synthesis of perovskite single crystals

Diego IGLESIAS and Victor SANS

POSTER No. 40

Sonochemically synthesized cobalt oxide nanoparticles as an additive for natural polymer iodide electrolyte based dye-sensitized solar cells

Zhi Ling GOH, Norshahirah M. SAIDI, N.K. FARHANA, Shahid BASHIR, Javed IQBAL, Ramesh KASI, Ramesh SUBRAMANIAM, Swelm WAGEH and Abul KALAM

POSTER No. 41

Optimization of the Oxygen Evolution Reaction through electron spin control in photoelectrochemical water splitting

Miriam GUNI, Wilbert MTANGI, Clemence SUMANYA, Rufaro KAWONDERA and Stephen NYONI

POSTER No. 42

Chiral metal organic frameworks in photoelectrocatalytic water splitting

Rufaro B. KAWONDERA, Wilbert MTANGI, Stephen NYONI and Gift MEHLANA

POSTER No. 43

SuperCapattery: Trump card of NexGen Vehicles

Pershaanaa MANOGRAN, Shahid BASHIR, Ramesh KASI and Ramesh SUBRAMANIAM

POSTER No. 44

Ion beam induced modification of structural, optical and electrical properties of polyprrole-methylammonium tin iodide (PPy-MASnI₃) nanocomposite films for photovoltaic applications

H.A. MNGOMEZULU, L.F. MABENA and M. MSIMANGA

POSTER No. 45

Preparation, characterization, and electrochemical evaluation of nickel sulphide on lignin-derived carbon material for supercapacitors

V.M. MOAGI, L.F. MABENA and M.V. MAPHORU

POSTER No. 46

Investigations of Earth Abundant Materials based Metal Oxide Photo-Electrodes for Solar Energy Conversion

Nabila NAWAZ, Linh TRINH and Renata SOLARSKA

POSTER No. 47

Complex processing of high-silicate phosphate ore in the scheme with recycling

I.B. SIBIRYAKOVA

POSTER No. 48

pH based supercapacitors: Achieving high capacitance in gold metallized regenerated cellulose amide supercapacitor electrodes by pH gradient

Oluwaseyi D. SALIU and James RAMONTJA

POSTER No. 49

Stabilization of compressed earth blocks (CEB) by pozzolana based phosphate geopolymer binder: physico-mechanical and microstructural investigations

Rolande Aurelie TCHOUATEU KAMWA, Sylvain TOME, Christoph JANIAC and Marie-Annie ETOH

POSTER No. 50

3D Printable Liquid Crystal Elastomers with Light-Induced Shape Transformations

Karl Albright TISTON, Voravee P. HOVEN and Benjaporn NARUPAI*

4. HEALTH

POSTER No. 67

Characterization of *Archachatina marginata* and *Achatina fulica* slime and determination of their antimicrobial activities

Racheal ABIODUN and Oluwasayo OGUNJINMI

POSTER No. 68

Fatty acids-based Eutectic Solvents Liquid Membranes for Removal of Sodium Diclofenac from Water

João AFONSO, Gabriela CAETANO and Isabel MARRUCHO*

POSTER No. 69

Caffeine tablet formulation targeted at a delayed drug release profile

Monsuru AIYEDUN, Mgambi GAMBA, Zahraa AJAMI and Rim EZZEDDINE

POSTER No. 70

Nanoemulsified Phytocapped Nanoparticles as Novel Antibiotics

Israel DAVID, Samson ALAYANDE, Fatai OLADOYINBO and Enok DARE

POSTER No. 71

Carbon nanotube-supported iron oxides enhance pollutant removal in wastewater

Giovanni SABOIA, Gustavo CHACÓN, Marcos VASCONCELLOS and Maria do CARMO RANGEL

POSTER No. 72

Human health risks associated with organochlorine pesticides level in soils in Eket agricultural zone, Akwa Ibom State, Nigeria

Akwaowo INYANGUDOH, Edu INAM, Ekeoma OGWO, Nnanake-Abasi OFFIONG, Treasure AWA-ARUA, Imeobong UDOEKPO and Crispin HALSALL

POSTER No. 73

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

M.T. MAZIBUKO, T.H. MOKHOTHU, P.S. MDLULI and Vimla PAUL

POSTER No. 74

Molecular Imprinted Polymers (MIPs) for selective extraction of Per- and Poly-fluoroalkyl substances (PFA) from water systems.

Nompumelelo MALATJI, Anele MPUPA, Boris MIZAIKOFF and Philiswa NOMNGONGO

POSTER No. 75

Electro photocatalytic degradation of organic pollutants over Ce doped-CaTiO₃ nano-perovskite

O.A. MTALANA, L.F. MABENA, M.V. MAPHORU

POSTER No. 76

Synthesis, DNA Base-Binding Properties and Anti-Oxidant Capabilities of Tetraaza Macrocyclic Ligand and its Ni Complex

Emmanuel C. OHAEKENYEM and Ikenna ONYIDO

POSTER No. 77

Synthesis of Chitosan/Ag₃PO₄/PtCl₆²⁻ as Photocatalyst for Methyl Orange Degradation

Rini LARASATI, Uyi SULAEMAN and Mardiyah KURNIASIH

POSTER No. 78

Boron complexes of dipyrromethenes, BODIPYs

Victoria Eirini Glypti

POSTER No. 79

Synthesis and Activity of Photocatalyst Composite defect-Ag₃PO₄/g-C₃N₄/PtCl₆⁻ For Degradation of Rhodamine B Dyes and Antibacterial Agents

Yusuf Mathiinul HAKIM and Uyi SULAEMAN

5. FOOD SAFETY

POSTER No. 80

Novel microspheres based on alginate/chitosan- nanocomposites as delivery vehicles of omega-3 rich oils

Ayat F. HASHIM, Said F. HAMED, Hoda A. ABDEL HAMID, Kamel A. ABD-ELSALAM, Iwona GOLONKA, Witold MUSIAŁ, Ibrahim M. EL-SHERBINY

POSTER No. 81

Precision in shoats selection using telomeres

Mercy MULANDI, Rawlynce BETT and Joseph JUNG'A

POSTER No. 82

Interpolyelectrolyte complexes based on polydiallyldimethylammonium chloride and sodium polystyrenesulfonate as a potential material for creating safe for health and effective antibacterial coatings for food safety

Vladislava PIGAREVA, Valeria MARINA, Anastasia BOLSHAKOVA and Andrey SYBACHIN

6. CLIMATE CHANGE

POSTER No. 83

Assessing circular processes using new tool of NCCPCT

Mohammed Mazen HARIRI, Sinan AL-JALALI and Moustafa Sayem EL-DAHER

POSTER No. 84

The role of C-scorpionate metal complexes for the conversion of CO₂

Inês MATIAS, Ana RIBEIRO and Luísa MARTINS

POSTER No. 85

Innovative processes for recycling multicomponent packaging materials

R. MASTRODDI, M. VAGNONI, W. PITACCO, C. SAMORÌ, P. GALLETTI and E. TAGLIAVINI

POSTER No. 86

Development of new homogenous catalysts for CO₂ reduction to formates

Asanda C. MATSHEKU, Chris MAUMELA and Banothile C.E. MAKHUBELA

POSTER No. 87

Design and synthesis of novel Lanthanide based metal-organic frameworks (MOFs) for catalytic hydrogenation of carbon dioxide to formic acid

Maureen GUMBO and Gift MEHLANA

POSTER No. 88

Primary, Secondary, and Tertiary sewage sludge pyrolysis for sustainable energy

Lyvia MENEZES, Edgar SILVEIRA, João MAZZONI, Rafael EVARISTO, Juliana RODRIGUES, Giulia LAMAS, Grace GHESTI and Paulo SUAREZ

POSTER No. 89

Biopolymeric Based Electrochemical Cell for the Removal and Recycling of Toxic Solvents from Pharmaceutical Effluents

Anita S. MRAMBA, Peter P. NDIBEWU and Linda L. SIBALI

POSTER No. 90

Green fuels production from waste oil

Patricia REÑONES, Diana GARCÍA-PEREZ and Jose M. CAMPOS-MARTIN

POSTER No. 91

Thermal exploitation strategies for paper mill waste

Rosaria LORE, Guido PASQUINI, Maurizio GIORDANO, Claudia ANTONETTI, Nicola DI FIDIO, Sara FULIGNATI, Domenico LICURSI and Anna Maria RASPOLLI GALLETTI

POSTER No. 92

Nanostructured Cu-based Catalysts Electrochemically Synthesized on a Carbonaceous Gas Diffusion Layer for CO₂ Electroreduction

M. SERAFINI, F. MARIANI, A. FASOLINI, E. SCAVETTA, D. TONELLI and F. BASILE

1. NEW REACTION PATHWAYS

Asymmetric poly(ionic liquid)–ionic liquid membranes for gas separation

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Non-solvent induced phase separation (NIPS) is one of the most used techniques to produce polymeric membranes from a wide variety of polymers. Nevertheless, this method has never been employed before in the preparation of poly(ionic liquid) (PIL)-based membranes [1-2]. The use of PILs and their derived materials incorporating ionic liquids (PIL–IL) has emerged as a highly promising strategy to design dense membranes with improved CO₂ separation [3-4]. In this context, considering that membrane thickness is a critical parameter for their industrial scale application, this study is a step forward in the preparation of integral asymmetric PIL–IL membranes, with a top dense thin layer and a bottom porous layer. Solutions of poly([Pyr11][NTf₂]) PIL and 20 wt% of [C₄mpyr][NTf₂] IL in acetone/dimethylformamide and acetone/formamide mixtures were prepared. The effect of several parameters of phase inversion process, namely, casting solution concentration and evaporation time, on the morphology (Figure 1) and gas separation performance of the resulting asymmetric PIL–20 IL NTf₂ membranes, was evaluated and compared to those of dense PIL–20 IL NTf₂ membrane. The results indicate that the choice of the appropriate solvent mixture strongly impacts membrane morphology and gas separation properties.

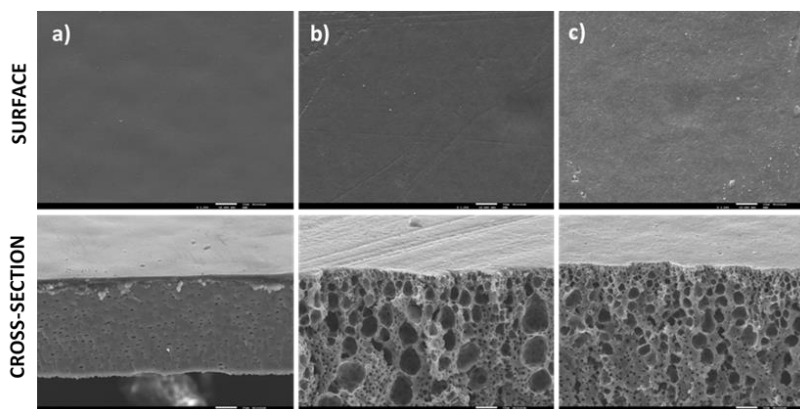


Figure 1. SEM images of PIL–20 IL NTf₂/acetone: dimethylformamide membranes at solvent ratios of 80:20 and casting evaporation times of (a) 1, (b) 5 and (c) 10 min.

From SEM analysis, it was shown that the type of co-solvent used, dimethylformamide or formamide, as well as, different evaporation times strongly influenced the PIL–20 IL NTf₂ membrane morphology. Regarding the CO₂ permeances of the resulting asymmetric PIL–20 IL NTf₂ membranes a significant

increase was observed. In particular, for PIL–20 IL NTf₂/acetone: formamide (85:15) membrane a 10-fold increase in CO₂ permeance was obtained compared with dense membranes, whereas only a small decrease in selectivity was observed.

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A multi-gram synthesis to pure HMF and BHMF

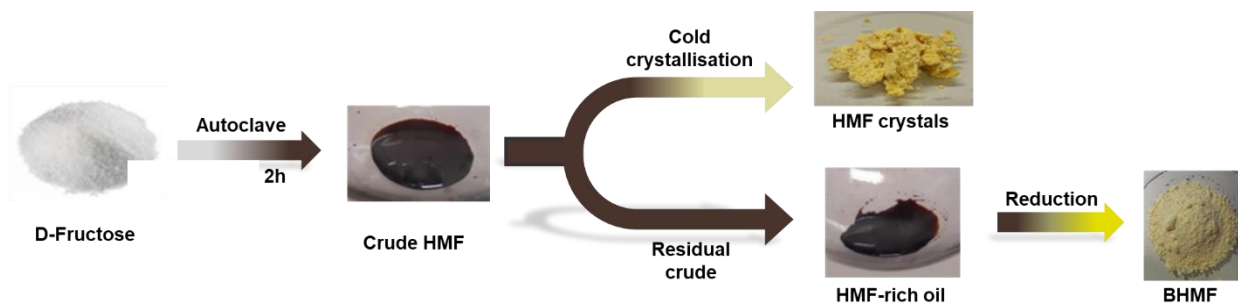
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5-Hydroxymethylfurfural (HMF) is a bio-based platform chemical that can be used as building block to produce complex and useful compounds with diverse applicability, in particular, bio-based polymers, materials and fuels [1], [2]. Even though HMF synthesis holds promise for a greener future, with the current state of technology the high production cost limits its competitiveness at an industrial scale[1]. In this project our main goal is to optimize yield and selectivity for the synthesis of HMF that will allow us to perform scale-up reactions with competitive yields with a green mindset. HMF synthesis was accomplished reacting D-Fructose with a heterogeneous acid catalyst in an adequate solvent system in a stainless-steel autoclave. Under these conditions it was possible to scale up the HMF production up to 40g of D-fructose as starting material. The final product was recovered from the crude mixture and purified by a custom-made crystallization procedure obtaining HMF crystals and a residual insoluble HMF-rich oil that can further reacted to produce BHMF. Finally, green metrics were used to evaluate the greenness of the reaction in comparison with previously reported works[3].



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Thermal reactions of cyclohexen-1,3-oxazine and 1,3-thiazine cis-fused cyclohexen-1,3-oxazines studied from green metrics

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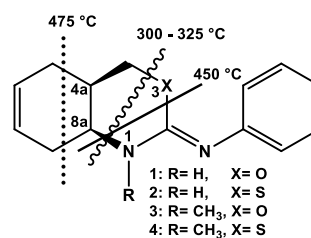
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The study of the thermal reactions of 1,3-oxazines and 1,3-thiazines is of great interest due to the different pharmacological properties of these compounds.^{1,2} In order to obtain information on the thermal stability of *cis-cyclohexen-fused* 1,3-heterocycles,^{3,4} as compounds **1**, **2**, **3** and **4** present in Figure 1, *flash vacuum pyrolysis* (FVP) reactions between 300-500°C were carried out. In addition to these reactions, a green assessment was carried out to identify the impact of the study of pyrolysis reactions on the environment. This study was carried out using two recognised methodologies for this evaluation, namely Green Star^{5,6} and Ecoscale⁶. Table 1 presents the results of the Green metric assessment of 1,3-oxazine and 1,3-thiazine compounds.

Table 1. Green parameters of 1,3-oxazine and 1,3-thiazines studied.

Sust.	Yield % ^a	GSAI%	EcoScale	MI	RME	AE	E
1	100	75,50	81	2,6	82	76,62	2,0
2	54,30	65,00	58,15	3,5	45,3	77,86	2,5
3	54,90	66,25	58,45	2,3	40,23	79,06	3,2
4	5,60	75,50	33,8	5,6	3,20	77,67	2,0

Figure 1.



^apercentage yield of pyrolysis product after isolation and purification, calculated at 475°C.

The Arrhenius parameters characterising these thermolysis processes show that: -the E_a and ΔH^\ddagger for the N-substituted compounds are higher than for their hydrogenated counterparts, -all processes occur with negative entropic changes, -due to the high temperatures employed, the entropic term is not negligible and the reaction mechanism must be proposed as a function of the ΔG^\ddagger , the observed differences in the ΔG^\ddagger allow multiple competitive reactions to be proposed, of which the retro Diels Alder reaction (RDA) is the most interesting from a mechanistic point of view.

In the evaluation of the thermolysis table 1, it was determined that the reaction conditions in which the principles of green chemistry are best fulfilled, is the use of substrate 1, since it presents better

values of atomic economy, low production of residues and derivatization. On the other hand, the low use of solvents for the isolation and purification of the products is highlighted. Similarly, it should be noted that in PVP processes, energy expenditure is minimised by the minimal or almost non-existent use of solvents or purification methods, since the reactions studied present only one product in general, and a similar reaction mechanism.

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A Further Step to Sustainable Hydroformylation

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There is a need to develop processes and products that are efficient and at the same time reduce and/or minimize the impact while still meeting the basic needs of the planet. The chemical industry must undergo a reformulation to achieve these goals. The hydroformylation reaction is an important chemical transformation which is industrially used to produce aliphatic aldehydes [1]. Aldehydes and their derivatives are widely present in society daily life and will be present for a long time. Aiming to attend the principles of green chemistry, we explored two areas capable of making the hydroformylation process more sustainable: (i) the use of green solvents, and (ii) the use of non-noble metal catalysts.

Solvents play a fundamental role in the overall process sustainability. Although several innovative solutions have been proposed recently, fossil-derived solvents traditionally dominate the scenario. Based on the modern solvent selection guides, we evaluated various green solvents in the hydroformylation reaction. Anisole demonstrated the best performance and was applied in the hydroformylation of several types of olefins, including bio-renewable terpenes. The results have shown that anisole is an interesting solvent for this transformation, allowing to match catalytic efficiency and process sustainability [2].

Next, we turned our attention to the alternative catalyst. Nowadays, the majority of industrial processes involve rhodium phosphine or phosphite complexes as catalysts. An interesting alternate which has been already applied in this transformation could be cobalt. We investigated the hydroformylation catalyzed by cobalt complexes. It has been shown that in the presence of phosphine oxides (in particular, triphenylphosphine oxide, a simple and low-cost substance), cobalt-based catalysts can act beneficially in the hydroformylation of olefins. The transformations take place under much milder conditions as compared to traditional processes. The presence of phosphine oxides dramatically facilitates the pre-activation of the cobalt pre-catalyst, saving time and energy. A wide range of products have been successfully prepared, in particular, from the substrates containing various functional groups. In addition, anisole, a solvent with a high degree of sustainability, can be advantageously used in these processes [3].

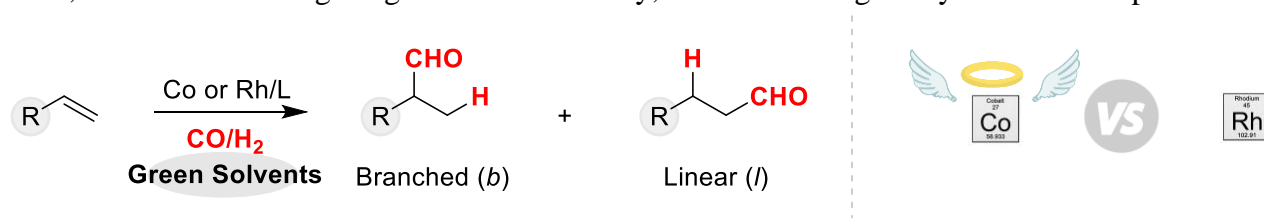


Figure 1. Hydroformylation: Green solvents and Cobalt vs. Rhodium.

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Metal phosphide nanoparticles for the hydrotreatment of methyl laurate to produce green liquid fuels

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The production of green diesel by catalytic deoxygenation (hydrotreating) of waste vegetable oils could have a great impact on the transition to a circular economy, less dependent on fossil fuels and less polluting. One of the most promising active phases for hydrotreatment processes are transition metal phosphide nanoparticles (NPs). This work aims to test the activity of catalysts based on phosphide NPs supported on silica in the hydrodeoxygenation of methyl laurate (model compound for waste oils). The green chemistry principles fulfilled are atom efficiency, preferably renewable raw material, catalytic rather than stoichiometric reagents, safer products by design and innocuous solvents and auxiliaries.

Ni and Ni-Mo phosphide NPs ($\text{Ni}_{1.6}\text{Mo}_{0.4}\text{P}$ and Ni_2P) have been synthesized by a facile molecular precursor route [1] and characterized by chemical analysis, TEM and XRD. TEM analysis indicates the formation of spherical NPs with a narrow distribution. XRD results showed that the peaks of the Ni_2P phase were shifted to a lower Bragg angle, indicating an expansion of the crystal structure due to the insertion of Mo in the structure. These results suggest the formation of bimetallic metal phosphides NPs. The NPs were incorporated into silica support by incipient wetness impregnation of NPs solution. A reference MoP/SiO_2 catalyst was prepared by wet impregnation on silica using Mo and P precursors dissolved in water followed by in situ reduction to form the phosphide [2].

The prepared catalysts were tested in the hydrodeoxygenation (HDO) of methyl laurate to hydrocarbons at two different reactant flows and temperatures (Figure 1). Ni_2P and $\text{Ni}_{1.6}\text{Mo}_{0.4}\text{P}$ catalysts showed low catalytic activity at both temperatures and flows whereas MoP and Ni_2P were very active catalysts. The comparison of activity between Ni phosphide monometallic catalyst and Ni-Mo bimetallic catalysts prepared by the molecular precursor route points out a synergy for bimetallic catalyst with a certain Ni-Mo ratio. With increasing the temperature from 300 up to 350°C the activity of all the catalysts increased but showed a clear deactivation with reaction time. With decreasing the space velocity from $\text{WHSV} = 5.22 \text{ h}^{-1}$ ($\text{LHSV} = 6 \text{ mL/g/h}$) to $\text{WHSV} = 2.61 \text{ h}^{-1}$ ($\text{LHSV} = 3 \text{ mL/g/h}$), the activity of all the catalysts also increased but less than with the increase of the temperature.

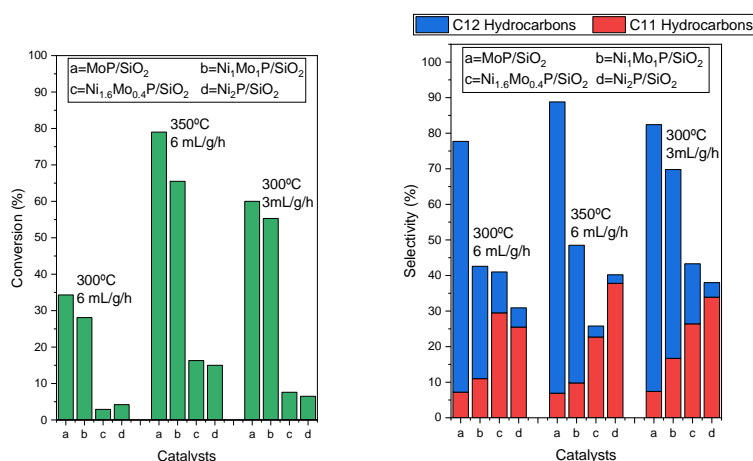


Figure 1. Average conversion and selectivity for HDO of methyl laurate.

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Reactivity of Ruthenium Acetylide Complexes Towards Carbon Dioxide

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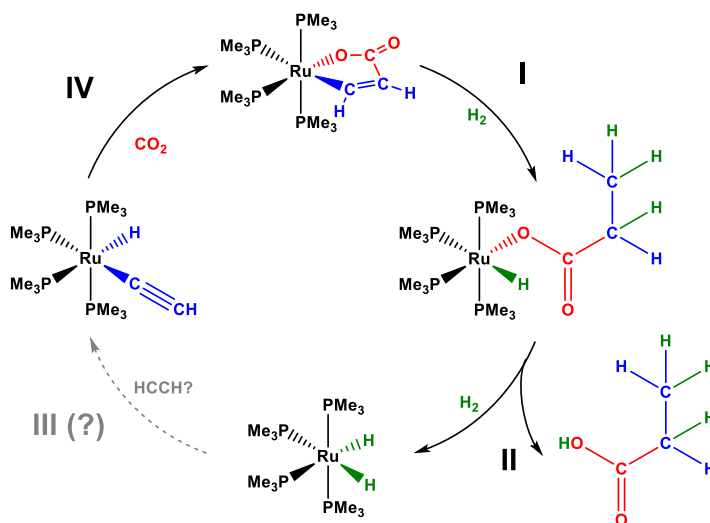
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The research project aims to develop catalysts which can couple CO₂ to an inexpensive substrate to produce value-added products. The importance of developing ways to productively utilize CO₂ is becoming more and more evident as atmospheric CO₂ levels continue to rise. Previous research has reported the catalysis potential of *trans*-[FeH(C≡CH)(depe)₂] for coupling CO₂ to acetylene (HC≡CH) to give propiolic acid (HC≡C(C=O)OH). [1] [Ru(η²-C₂H₄)(P(CH₂CH₂PPh₂)₃)] has been reported to couple CO₂ to ethylene to give potassium acrylate (KOC(=O)CH=CH₂), with a modest TON.[2]

CO₂ reacts with ruthenium metal acetylides to produce metallalactones. We have been investigating the use of hydrogen as a potential agent to cleave the lactone-type ligand from [Ru(OC(=O)CH=CH-κ²C,O)(PMe₃)₄]. Preliminary results indicate that this occurs via the initial hydrogenation of the metallalactone complex and hydrogenolysis of the metal-carbon bond to produce a novel hydrido propionate complex (Figure 1, Step I). Further hydrogenolysis liberates propionic acid and produces the *cis*-RuH₂(PMe₃)₄ complex (Figure 1, Step II) We are currently looking into ways of converting the *cis*-RuH₂(PMe₃)₄ complex into *cis*-RuH(CCH)(PMe₃)₄ (Step III). *Cis*-RuH(CCH)(PMe₃)₄ is known to rapidly react with CO₂, to give the starting metallalactone complex (Step IV).

Figure 1. Proposed catalytic cycle. Steps I, II and IV have been shown to work while a method for performing step III is still under investigation.



Acknowledgements:

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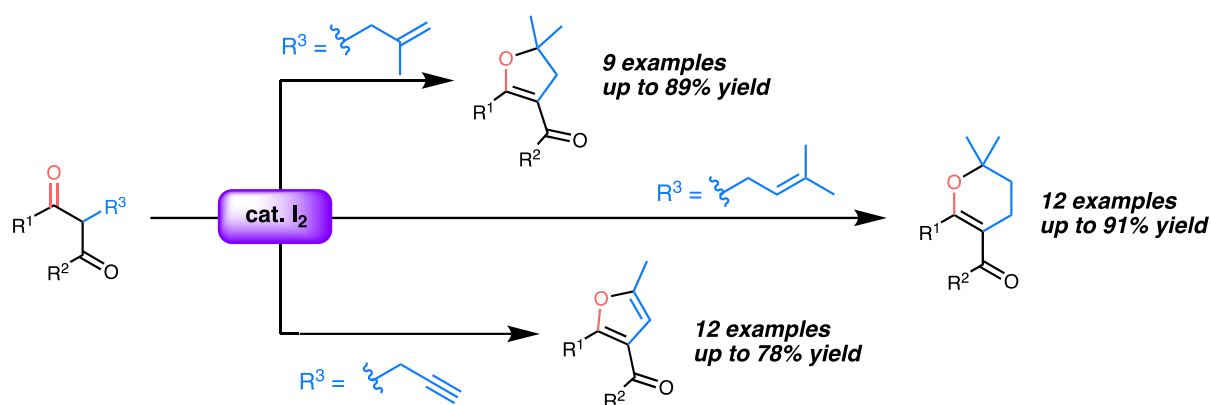
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Exploring Mechanisms in Iodine Catalysis

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Molecular iodine is a cheap, environmentally benign, non-toxic commodity chemical. It has already proven to be an excellent catalyst for a wide variety of organic transformations, however full realisation of its catalytic potential requires systematic and comprehensive mechanistic investigations.¹ This work investigates how molecular iodine catalyses the formation of pyrans and furans with thorough computational and experimental mechanistic investigations, to pave the way for increased use of this operationally simple, green, and non-toxic catalyst.²

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Sustainable Gold Extraction via Host-Guest Chemistry

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Gold extraction is conventionally achieved with toxic cyanide and mercury. Thus, more sustainable methods for gold extraction are imperative not only for the prevention of environmental disasters, but also the well-being of those working in gold mines. Host-guest chemistry may be the key to solving this problem. This research builds on previous studies which discovered the spontaneous precipitation of gold species with environmentally friendly cyclodextrin macrocycles through the formation of host-guest complexes.¹⁻²

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Research on the preparation of mono-benzene aromatic compounds by catalytic hydrogenolysis of lignin

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As the only renewable organic polymer containing benzene rings, lignin has gradually attracted the attention of researchers due to its potential to replace fossil energy such as coal and petroleum, and the proposal and realization of the concept of "carbon neutrality and carbon peaking." At present, the scientific research community generally believes that three monomers make up lignin, namely p-coumarol (H), coniferyl alcohol (G), and sinapyl alcohol (S). However, in the process of catalytic conversion using lignin as raw material, derivatives of these three monomers or other benzene ring-containing compounds are often obtained. The solubility of lignin in solvent and the selectivity of products are the premise of further study on the structure of lignin and its transformation and utilization. Aromatic compounds play an important role in the fields of fragrances, flavors, polyesters, etc. Catalytic hydrogenolysis of single benzene ring aromatic compounds from non-fossil-based raw material lignin is an important way to meet the needs of human beings for the production and production of benzene ring-containing compounds.

In this paper, organic soluble lignin (2.0 g) was used as raw material, tetrahydronaphthalene (20.0 g) was used as the hydrogen-donating solvent, without or with (MoS_2 or Ru/C) catalyst, and the reaction temperature was 400 °C, and the initial hydrogen was 4.0 MPa. pressure reacted in a high temperature and high-pressure reactor for 6 h, and finally obtained a thick black, brown-black, or green apple color reaction mixture, respectively. The solution to be tested and the filter residue is obtained by sequentially performing centrifugation, suction filtration, rotary evaporation, and membrane filtration on the reaction mixture. Then, a qualitative analysis of the liquid to be tested was carried out by GC-MS. Based on the

above basic experimental research, the following conclusions are drawn: (1) Catalytic activity: with catalyst (Ru/C > MoS₂) > without catalyst; (2) Relative content of products: Ru/C > MoS₂ > without catalyst; (3) Product Type: When there is no catalyst, the conversion rate is 90.4%, and mainly to obtain small molecular fragments of lignin liquefied lignin, resulting in high conversion rate and dark color of the reaction solution and less light oil components (GC-MS only detected a very small amount of cyclohexane, methylcyclohexane, toluene, ethylcyclohexane, phenol and other phenol derivatives). When MoS₂ catalyzed the reaction, the conversion rate was 86.8%, mainly to obtain lignin liquefied lignin small molecular fragments (no more catalyst time), resulting in a slightly lower conversion rate and a brownish-black color of the reaction solution and relatively more light oil components (the substances detected by GC-MS are mainly benzene, ethylbenzene, propylbenzene and a small amount of other phenol derivatives). when Ru/C catalyzed the reaction, the conversion rate was 43.4%, and a very small part of lignin was liquefied into lignin small molecular fragments, resulting in the smallest conversion rate and the color of the reaction solution was green and transparent, and more small molecular compounds such as cyclohexane, methyl cyclohexane, toluene, o-dimethylcyclohexane, ethylcyclohexane, ethylbenzene, p-methylethylbenzene, p-xylene, propylcyclohexane, propylbenzene, ethylcycloheptatriene, butylcyclohexane and other phenol derivatives; (4) The ability of lignin hydrogenolysis to mono-benzene ring aromatic compounds: Ru/C > MoS₂ > no catalyst.

From this, it can be concluded that a catalyst is necessary when preparing mono-benzene ring aromatic compounds by one-step hydrogenolysis of lignin, and the choice of catalyst is also an important factor to be considered. In our study, Ru-based catalysts were found to have obvious catalytic effects. In the future, improving on Ru-based or other noble metal (such as Pt, Pd, Rh, Ir, etc.) catalysts is an effective way to hydrogenolysis lignin.

Design, Synthesis and Characterization of Iridium(III), Ruthenium(II) and Palladium(II) Complexes and their Evaluation in the Hydrodeoxygenation of (E)-6-(furan-2-yl)-4-oxohex-5-enoic acid

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Reduced Schiff base ligands have gained a lot of attention in complex synthesis.¹ This is due to their flexibility and ability to easily form 5 - 6 membered rings upon complexation.² Schiff base ligands are known to control the activity of metals in different transformations, this is owed to their ability to stabilize metals in different oxidation states.³ As a result they have been widely used in homogenous and heterogenous catalytic reactions.⁴ In this work, a series of novel Ir^{III}, Ru^{II} and Pd^{II} N,N schiff base complexes and their reduced counterparts were synthesized. These complexes were characterized using multi-dimensional nuclear magnetic resonance, infrared spectroscopy, mass spectrometry, elemental analysis and single crystal x-ray diffraction. The reduced counterparts displayed excellent thermal, air and moisture stability. Preliminary catalytic experiments were performed and exhibited good catalytic activity in the hydrodeoxygenation of model substrate (E)-6-(furan-2-yl)-4-oxohex-5-enoic acid. Over 98% conversion was achieved under the optimum conditions.

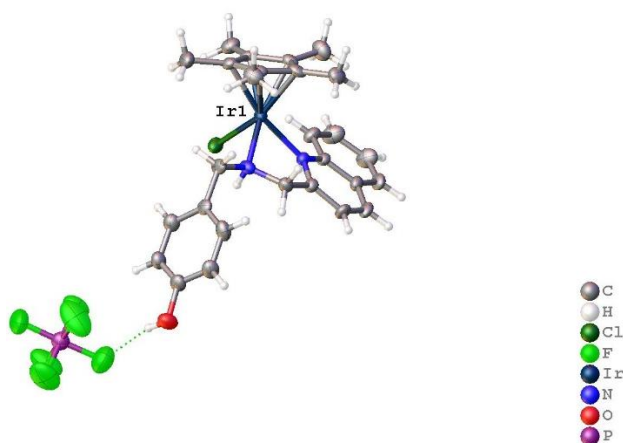


Figure 1 Molecular structure of reduced Schiff base complex for HDO of bioderived

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Catalytic hydrosilylation of alkynes and imines in green solvents

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Hydrosilylation reaction is the commonly used transformation in organosilicon chemistry in the synthesis of various silylated saturated and unsaturated compounds, e.g., silylated olefins, alkanes, amines or alcohols, which are valuable building blocks in organic synthesis.¹

Hydrosilylation of alkynes provided silyl substituted olefins that might be further used in the C-C reactions or desilylation processes. Reduction of imines with silanes, followed by the hydrolysis of obtained products yields functional amines, which are important synthons for the production of pharmaceuticals or agrochemical.² Reduction with silanes, due to the milder reaction conditions and safety reasons in comparison to hydrogenation reactions creates the alternative for the synthesis of these valuable compounds. To obtain high process chemo-, regio- and stereoselectivity the homogeneous catalysts based on noble metals are required. Despite the activity and selectivity of traditional homogeneous catalytic systems, catalyst recycling and limited stability are still key issues that require further optimization to increase the applicability of these reactions.³

In this communication, we would like present our recent research on the application of green solvents like, supercritical CO₂ (scCO₂) and ionic liquids (ILs) for the hydrosilylation of alkynes and imines.^{4,5} Such strategy increases process sustainability by the reduction or elimination of typical, toxic organic solvents used for maintenance of homogeneous conditions and for products separation. Moreover, they allow catalyst immobilization, increase TON and TOF values and simplify products separation, by extraction in the CO₂ stream. Several commercially available Pt, Ru and Fe catalysts were applied in hydrosilylation of alkynes and imines in conventional or green solvents, the screening of the reactions conditions and reagents on products selectivity will be also discussed.

Acknowledgments: We would like to thank the National Science Centre (Poland), grant no. UMO-2018/31/G/ST4/04012, for financial support.

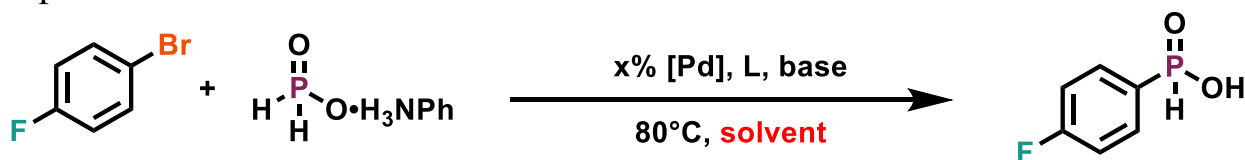
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A 'greener' route to monoarylphosphinic acids

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The phosphinic acid group is a valuable motif in the development of drugs and agrochemicals but is currently underutilised in organic synthesis.¹ Most phosphorus containing organic molecules are derived from phosphorus trichloride (PCl_3). PCl_3 is highly reactive, toxic, and is a precursor involved in making chemical weapons.² Hypophosphorus acid (H_3PO_2) is gaining traction as a valuable source of phosphorus for organic synthesis, as it is less toxic than PCl_3 , is commercially available as an air-stable solution in water, and forms bench stable salts. Herein we discuss the optimisation of a palladium catalysed mono-arylation of anilinium hypophosphite with aryl bromides to form arylphosphinic acids, which can serve as versatile building blocks for transformation into other phosphorus functional groups. This transformation is tolerant of many industrially preferred solvents, a 'green' step forward from previous methods which are dependent on DMF or THF.^{3,4}



Solvent choice: EtOAc, DMC, MEK, ⁱPAc

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GREEN OXIDATION OF PHENOLS AND NAPHTHOLS ON SILICA-SUPPORTED GOLD AND RUTHENIUM CATALYSTS

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Oxidation of phenols and naphthols is an important goal in fine chemical synthesis [1]. These reactions are essential for the formation biologically active compounds, which are central building blocks for many synthetic and natural products [2]. Quinones and binaphthones are known to play an essential role in medical and pharmaceutical sciences [2]. In this work, the green oxidation of phenols and naphthols was carried out using heterogeneous silica-supported Ru-Bi, Au-Ru and Au-Bi catalysts. The catalysts were prepared by microwave-assisted loading (MW) and impregnation (IM) methods and characterized for their physicochemical properties using N₂ physisorption, XRD, and SEM-EDX analysis. The catalysts were tested for the oxidation of trimethylhydroquinone and 4-methoxy-1-naphthol in methanol and/or nitromethane at room temperature and under reflux with “clean” hydrogen peroxide oxidant. In the oxidation of trimethylhydroquinone (**1**) [Scheme 1] in MeOH at r.t and 60°C on MW-Au-Ru catalyst, yields of 96.6% and 100% for trimethyl-1,4-benzoquinone were obtained, respectively. However, there was no reaction when MW-Au-Bi and MW-Ru-Bi catalysts were used under the same reaction conditions. When 4-methoxy-1-naphthol was used as a substrate over MW-Au-Ru catalyst at r.t., yields of 33.8% (Conversion: 34%) and 50.8% (Conversion: 99 %) for binaphthone in MeOH and MeNO₂, respectively. The selectivity of this reaction depends on the solvent, temperature and catalyst used.

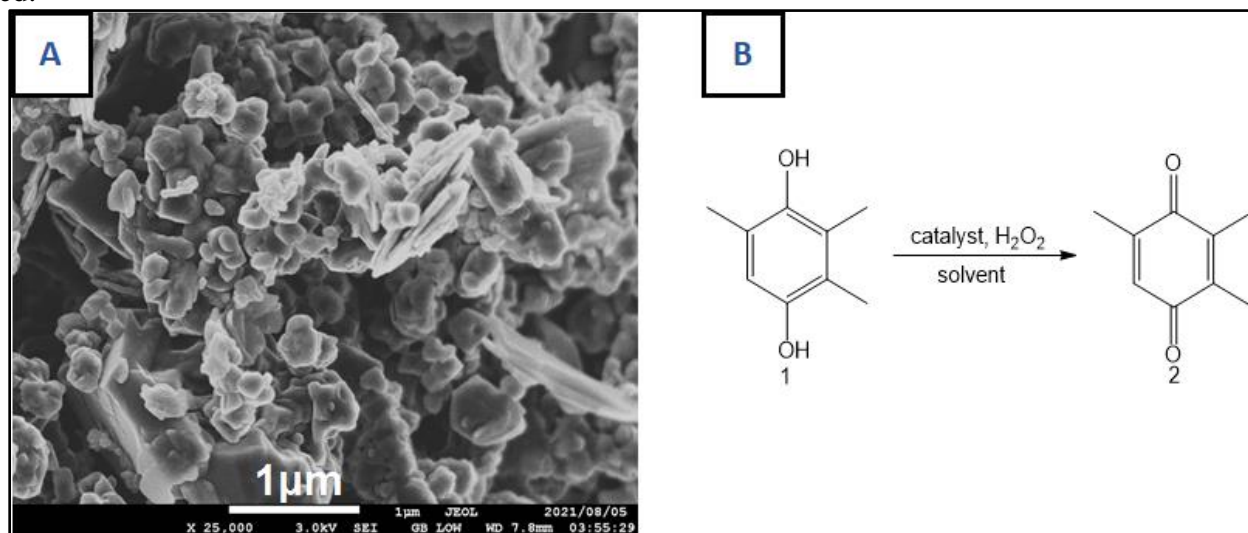


Figure 1: SEM image of Au-Ru-MW (a) Oxidation of trimethylhydroquinone on silica-supported gold and ruthenium catalysts (b).

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Eco-friendly Uracil Selenylation Employing I₂/DMSO as a Catalytic Oxidation System

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In this work, we are developing a new greener synthetic protocol for C5 uracil selenylation employing I₂ as catalyst in DMSO and diorganoyl diselenides in order to obtain the corresponding 5-organylselenyl uracils¹. The I₂/DMSO association has proved to be a simple, effective, metal-free and eco-friendly oxidative system with a wide range of applications in organic synthesis.² Besides, the reaction occurs without the use of any additional solvent – DMSO acts as an oxidant as well as a minimum solvent for this reaction. Uracil **1a** and diphenyl diselenide **2a** were selected as model substrates. After several optimization tests, we reached the best reaction condition (eq. (a), Figure 1) using I₂ in the catalytic amount of 10 mol% and 10 equivalents of DMSO at 100 °C for 3h, obtaining the desired product **3a** in 96% yield. Currently, other examples of uracil and derivatives are being tested under the best reaction conditions, including uracil-containing nucleosides. In all cases, good to excellent yields of **3** were obtained showing that this transformation has potential to become a new environmentally sustainable methodology for selenylation of this class of substances.

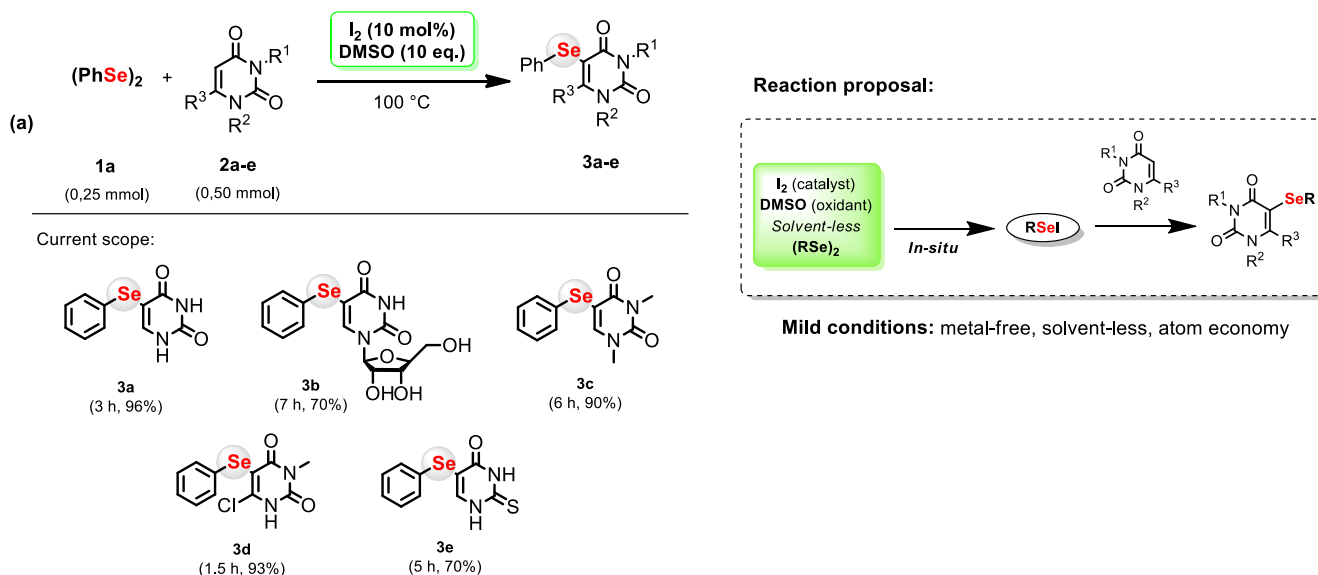


Figure 1. Uracil Selenylation Employing I₂/DMSO.

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Selective Cu and Ni-MOFs as pre-catalysts for the hydrogenation of furfural to furfuryl alcohol

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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 coordination networks.^{1,2} These materials have a high surface area, good stability, highly ordered structure, unprecedented structural tunability and are inexpensive.³ 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 and nickel MOFs have been synthesized and characterized using X-ray diffraction studies (powder X-ray diffraction, single crystal X-ray diffraction), and thermal analysis (thermogravimetric analysis, differential scanning calorimetry). The MOFs were evaluated as pre-catalysts using molecular hydrogen as a hydrogen source. These catalytic systems resulted in good activity and exclusive selectivity towards furfuryl alcohol in the hydrogenation reaction.

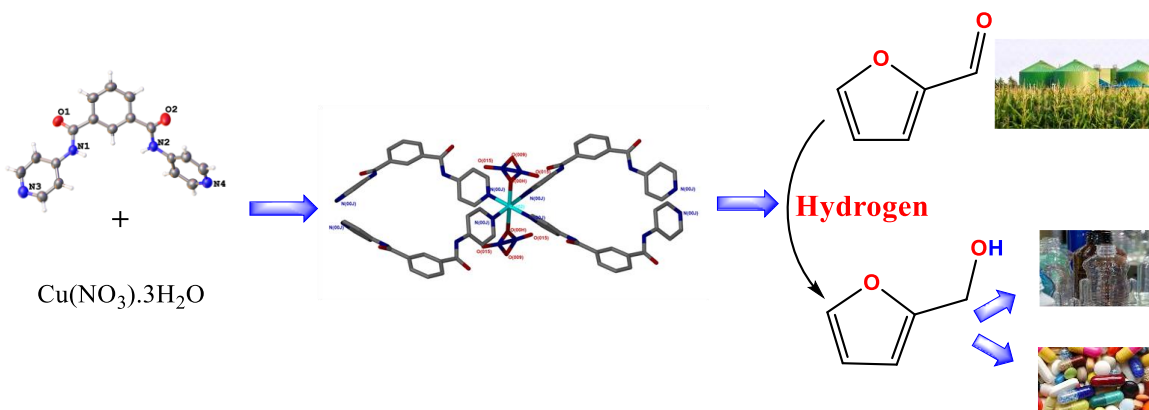


Figure 1. Graphical abstract.

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La(III) Schiff Base Complexes: Microwave-Assisted Synthesis, Physicochemical and Spectroscopic Analysis

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Schiff bases are the compounds with azomethine functional group (C=N) that formed through condensation reaction between primary amine with either aldehyde or ketone. This Schiff base can be easily coordinated with the various metal ions as chelating ligands, resulting in stable and brightly coloured metal complexes with fascinating physical, mechanical, biological and catalytic properties [1]. Nowadays, people keep concerned about green chemistry by focusing on the design of products and processes that minimize or eliminate the use and generation of hazardous substances. Microwave-assisted synthesis is one of the alternatives to produce compounds that fulfilled the green chemistry requirement by using microwave radiation to generate heat in a chemical reaction [2]. Moreover, this microwave-assisted synthesis (MW) become more popular due to the clean, cost-effective, and highly accelerated rate of reaction that helps to perform the reaction in much less time and good yields [3].

Two lanthanum(III) Schiff base complexes, 2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3-diyl)bis(azanylylidene))bis(methanylylidene))diphenollanthanum(III) [**La(AD1H)**] and 6,6'-((1E,1'E)-((2,2-dimethylpropane-1,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2-methoxyphenol)lanthanum(III) [**La(AD1OMe)**] were successfully synthesized (**Figure 1**). The complexes were prepared through microwave-assisted synthesis where a minimum amount of solvent was used and a shorter reaction time is taken compared to conventional reflux. Both ligands and their lanthanum(III) complexes were characterized through melting point, elemental analysis, FTIR and ¹H NMR spectroscopy. The shifting of the azomethine (C=N) band to a higher frequency, $\Delta\nu=17-18\text{ cm}^{-1}$ in IR spectra indicated that the complexation between ligands and metal centres has been established. It was further supported through the shifting of the azomethine proton signal to a higher chemical shift, $\Delta\delta=0.19-0.21\text{ cm}^{-1}$ in ¹H NMR spectra. The completion of reactions through the conventional method required 4.0 h while the MW method only took 8 min to complete the reaction. At the same time, the yields of products increased from 46.4–70.9% to 77.0–88.9%. In addition, less solvent was used in the MW method compared to conventional heating where the only half amount of solvent commonly used in the conventional method was used for MW synthesis. Moreover, the usage of water was unwanted in MW method. Hence, it will be more saving in terms of cost and environment. These results indicated

that the reactions through MW were completed in a shorter time with relatively higher yields compared to the conventional method [2].

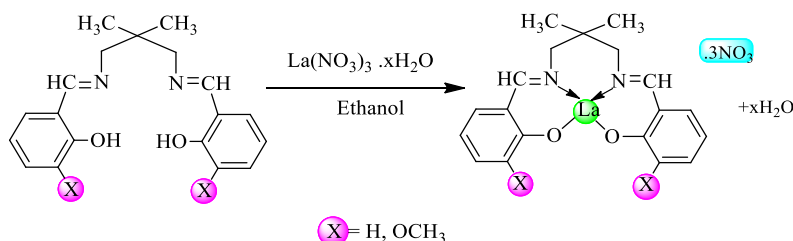


Figure 1. Synthesis of lanthanum(III) complexes

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Ethanol as a Green Solvent for the Catalytic Applications of a Heterobimetallic Compound in Tandem Transformations

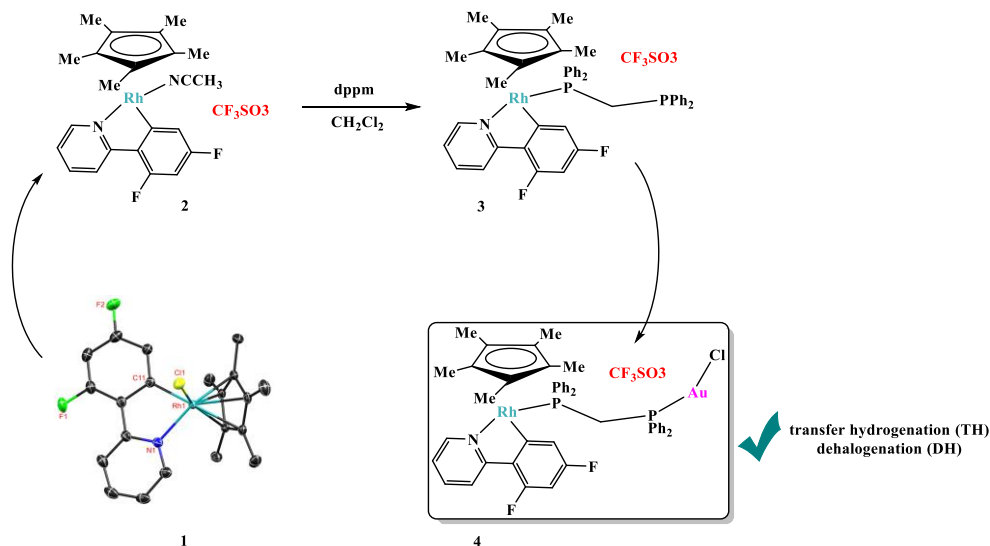
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Some reports about the most recent advances in using heterometallic catalysts based on single-frame N-heterocyclic carbene ligand¹. Tandem catalysis is a growing field that is beginning to yield significant scientific and technological advances toward new and more efficient catalytic processes². Additionally, ethanol can be introduced as a promising green solvent suitable for tandem reactions³.

The present study describes the synthesis strategy for the preparation of a new heterobimetallic Rh^{III}-Au^I complex, **4**, using 1,1-bis(diphenylphosphino)methane (dppm) as a linker ligand (Scheme 1) which is suitable for one-pot transfer hydrogenation and dehalogenation. By combining the catalytic properties associated with the two different metal centers, its application in the design of tandem processes makes the process shorter. It saves energy as the temporal purification is avoided³. This complex was characterized by utilizing several analytical and spectroscopic methods.



Scheme 1. Synthetic route for the preparation of heterobimetallic Rh^{III}-Au^I complex.

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The versatility of Acetamido-TEMPO in the chemical and electrochemical activated oxidation of alcohols

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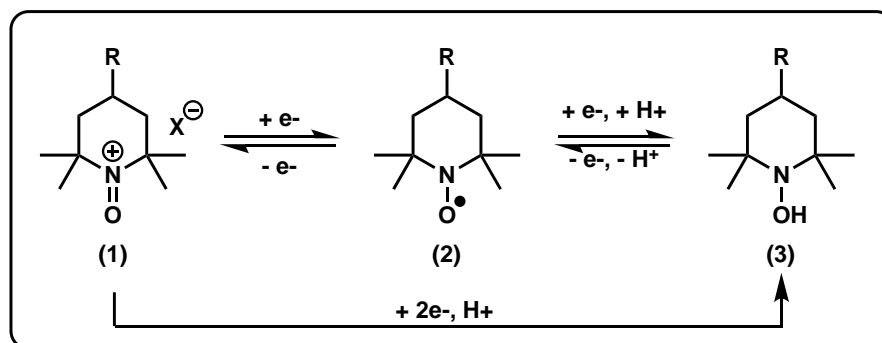
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Oxoammonium salts (1) have been broadly used as oxidants in a variety of transformations ranging from simple alcohol oxidations to more complex reactions such as oxidative amidations and esterifications.[1] Although its efficiency and ease to use, super-stoichiometric amounts of the salt are needed due to a comproportionation reaction between (1) and (3) to form two equivalents of (2). A more sustainable alternative is to employ its TEMPO-like radical precursor (2) as a pro-oxidant and a cheaper salt as a terminal oxidant.[2,3]

A simple and robust, metal-free route for the oxidation of trifluoromethyl alcohols and secondary alcohols to ketones is described. The methodology employs sodium persulfate as a primary oxidant and a catalytic quantity of 4-acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl (acetamido-TEMPO, ACT, (2) with R = NHAc), and it is applicable to fluorinated and non-fluorinated alcohols. Going one step beyond, some recent advances in electrochemical oxidations of alcohols by using ACT as mediator are shown. In this way the oxidation of alcohols to ketones and aldehydes can be reached in a greener fashion substituting a chemical terminal oxidant by just an externally applied electron current.



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Green synthesis of glycerol-derived surfactants for environmental applications

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Nowadays, with the continuous increase of the biodiesel demand significant amounts of glycerol are put on the market (2.5 Mt in 2020) and will represent one of the major worldwide drop-in chemicals for the near future. Among the various possibilities for the production of a wide spectrum of molecules (fine chemicals, commodities, fuel additives, specialties) starting from glycerol, the production of epichlorohydrin (ECH), mostly used in the production of epoxy resins, is an important industrial reality. As a matter of fact, Solvay started in 2011 the glycerol-based production of epichlorohydrin, the so-called Epicerol® process that actually supports the traditional process based on the chlorination of propene at elevated temperatures. Recently, we demonstrated that glycidol can be obtained as value-added product from this process [1]. Moreover, bio-based glycidol can be also obtained through glycerol deoxydehydration to allyl alcohol followed by epoxidation reaction [2-3].

We recently reported the conversion of the as-obtained glycidol to several chemicals of high concern as well as polymers [4], solketal [5], diols [6] and monoalkylglyceryl ethers (MAGEs) [7-9].

Other MAGEs of great interests are represented by surfactants when the aliphatic chain is in the range C8-C24. This class of compounds also respect the 10th principle of Green Chemistry because they are fully biodegradable in the environment and show a very low toxicity. Only few studies deal with long-alkyl ether synthesis, usable as bio-surfactants, from direct etherification of glycerol with fatty alcohols however this approach shows several drawbacks and very poor yields (lower than 15 %) and selectivity. In this work we report on the synthesis of monoalkylglyceryl ethers by glycidol alcoholysis with long-chain alcohols catalyzed by simple homogeneous metal triflates.

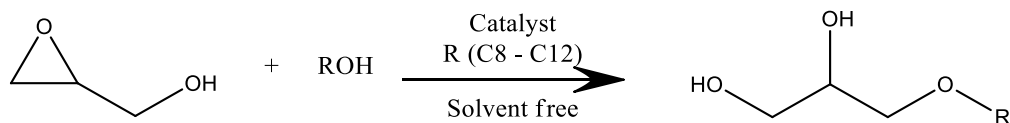


Figure 1. MAGEs synthesis through glycidol alcoholysis.

Moreover, we investigated the alcoholysis of glycidol with aryl alcohol (phenol and derivatives) in order to obtain mono aryl glyceryl ethers (MArGEs), products with high added value, being surfactants or drug precursors.

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Multicomponent reactions as a green strategy for syntheses of complex molecules

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To address the need for expeditious syntheses of novel compounds, multicomponent reactions (MCRs), defined as containing three or more reactants to afford one product, have been extensively explored over the last two decades. Indeed, MCRs have proven to be versatile tools delivering molecules with value spanning small molecules to macromolecules^[1–3] The deployment of MCRs not only enjoys atom, pot, and step-economy in the synthesis of complex and diverse molecular architectures but also aligns with green chemistry principles. Generally, more components lead to more complexity and are taken to an extreme “higher-order” MCRs, where six or even more components react in a one-pot, have been developed, although they remain scarce compared to their 3, 4 and 5-component relatives.^[4] Furthermore, the rich footprint of isocyanides in multicomponent reactions in particular has been fruitful in delivering higher order six to eight component reactions through mechanistically similar pathways. (Figure 1) In terms of green chemistry criteria, MCRs are versatile tools that have paved the way for the evolution of green chemistry aspects.^[5] Several “one-pot” syntheses, referring to chemical reactions conducted in a single reaction vessel, have led to outstanding efficiencies, waste diminution, and also decreasing steps and reaction vessels. Another greener aspect of the MCR strategy has been that harmful and toxic intermediates are produced in situ during the organic reactions, and the ensuing components in a vessel could be used for the synthesis of the next product. Last but not least, green metrics have been taken into account in MCR approaches such as atom economy or atom efficiency and the environmental impact factor (E-factor) which leads to elevated atom economy accompanied by a lower E-factor, as a reduced amount of waste product formation occurs.

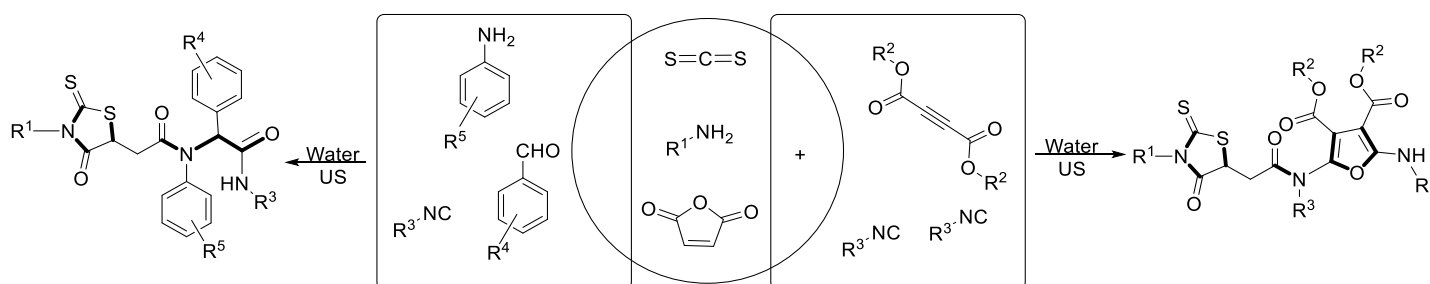


Figure 1. Six-component reactions for synthesis of rhodanine derivatives

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Conversion of CO₂ to value-added products through a CuZnO-Cu/Zeolite ZSM-5 hybrid catalyst

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The continuous concentration increase of CO₂ in the atmosphere and other greenhouse gases (GHG) produces in an average global temperature increase of the planet, strongly modifying the climate for natural systems [1]. Faced with this situation, it is urgent to stabilize the concentration of CO₂ in the atmosphere, which is why it is proposed to convert anthropogenic CO₂ into value-added products. Among the technologies to capture or transform CO₂ there are several already in mature stages, and it is worthy of mention that different technologies and processes use catalysts that are principally considered a pillar of green chemistry [2].

Based on this, we present the conversion of CO₂ to liquid fuels using CuZnO, Cu/Zeolite ZSM-5 catalysts and a CuZnO-Cu/Zeolite ZSM-5 hybrid catalyst. The CuZnO catalyst was obtained by impregnation and the Cu/Zeolite ZSM-5 catalyst by ion exchange, the hybrid catalyst is made by two bed in series, up of a CuZnO catalyst bed and a Cu/Zeolite ZSM-5 catalyst bed. After synthesis, the catalysts were characterized by SEM/EDS, XRD and TPR, where their main physicochemical properties were identified, which directly influence their activity, selectivity and stability.

The catalysts were evaluated in the CO₂ hydrogenation reaction in a fixed bed reactor, which was carried out at 250 °C, 3 atm and with a feeding gas flow of 10 mL/min of a CO₂/H₂ gaseous mixture molar ratio 1:3, and the analysis of the reaction products was performed by gas chromatography.

The preliminary results showed that the Cu/Zeolite ZSM-5 catalyst does not present activity in the hydrogenation of CO₂ to methanol, since no reaction product was obtained, on the other hand, with the CuZnO catalyst, it was presented a selectivity of 100% towards the formation of methanol. Finally, with the CuZnO-Cu/Zeolite ZSM-5 hybrid catalyst, formed by two beds in series, a selectivity of 5-10% for methanol and 90-95% to a second product was obtained. This result suggests that the methanol formed in the first CuZnO catalytic bed is converted into a second product with the Cu/Zeolite ZSM-5 catalytic bed, because the methanol concentration decreases as the concentration of the second product increases. In summary, in this case, the production of methanol is directly associated with the hydrogenation of CO₂ over the CuZnO catalyst, and the obtaining of the second product is associated with the transformation of methanol with the Cu/Zeolite ZSM-5 catalyst.

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Microwave-assisted synthesis of non-noble metal nanoparticles for plasmonic applications

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The extensive access to crystalline nanoparticles (NPs) is essential for many nanotechnology applications such as catalysis, drug conveyance, optoelectronics, attractive gadgets, medication, Materials science, and other interdisciplinary fields. {Jain, 2008, Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging, Sensing, Biology, and Medicine} The chemical synthesis of coinage and noble metal NPs (Ag, Au, and Pt) and their optical sensitivity in the visible region is quite well understood, but the optical sensitivity of metallic NPs in the ultraviolet (UV) regime has not been explored yet. Thus, it necessitates using other nanomaterials, such as aluminium (Al) which cover both visible and UV regions.[1],[2] The synthesis of a wide variety of AlNPs with varying morphologies while remaining mass-production and eco-friendly synthesis is still needed. In this work, we have utilized the non-conventional and green synthesis approach via microwave-assisted formation of NPs. A microwave synthesizer was used to synthesize non-noble metal plasmonic nanoantennas of Al which are cheap, light-weight, ease of preparation, and possess a tuned plasmonic range. Various parameters of transformation and microwave setup such as temperature, pressure, stirring, and reaction time were optimized to obtain different scaffolds of AlNPs, including porous ones. The synthesized AlNPs were thoroughly characterized by UV-visible spectroscopy, transmission electron microscopy, and field-emission scanning electron microscopy (Figure 1). The development of these size controllable and porous AlNPs would lead to promising applications in sensing and photocatalysis, which uses light in a broad range from UV to visible.

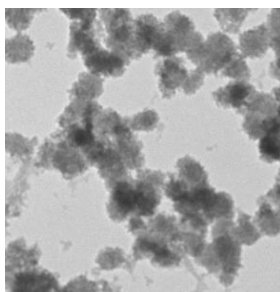


Figure 1 The synthesized porous aluminum nanoparticles using a microwave mediated synthesis method. The porous particles are about 100 nm in diameter.

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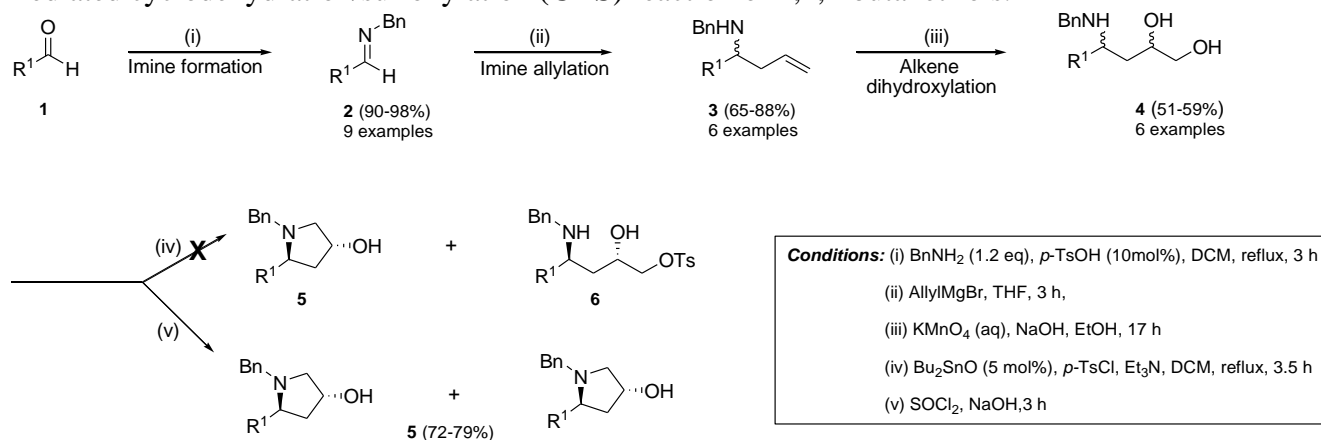
Stereoselective synthesis of functionalized pyrrolidines from aldehydes

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Small-ring heterocycles play an important role in drug discovery and appear frequently in drugs or prodrugs. According to Alien and co-workers, drugs containing pyrrolidines with a hydroxyl moiety have the potential to exhibit inhibitory activity against mycobacterium tuberculosis (*M.tb*).¹ Since South Africa has the third highest toll of global TB incidence, it is incumbent on local scientists to be involved in the search for new anti-TB drugs are needed to fight the epidemic.² The facile and environmentally friendly general synthesis of pyrrolidine compound could be an important asset to generate lead compounds. Thus, the key objective of this project was the application of a generic synthetic approach to produce a diverse library of pyrrolidines as shown in Scheme 1 based on the diastereoselective tin-mediated cyclodehydration/sulfonylation (CDS) reaction of 1,2,4-butanetriols.³



Scheme 1. General design for the synthesis of substituted pyrrolidines

Different oxidation/dihydroxylation methods were tried on the homoallylic amines (**3**) resulting in poor yields and decomposition. Ultimately a cold solution of KMnO_4 in basic medium (NaOH) oxidized the majority of **3** to the 4-amino-butanediols (**4**) in moderate yields (51-59%); homoallylic amines containing unprotected phenolic groups underwent decomposition. The CDS reaction failed to give either **5** or **6** and resulted only in *N*-sulfonylation. Pyrrolidines **5** were eventually obtained via a SOCl_2 induced cyclodehydration in good yields (72-79%); no stereoselectivity was observed since the diastereomeric syn/anti ratio established via HSQC was 1:1.

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Structural diversification of diterpenes through complementary peroxidic oxidations

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Natural products (NPs) are an important and essential source for research and discovery of new therapeutic agents.^[1] They have very different chemical properties from most synthetic compounds, which is why they are currently used as chemical precursors to obtain a wide variety of compounds with molecular diversity. To this end, one of the strategies used, called *Complexity to Diversity*,^[2] focuses on obtaining compounds through changes in the ring system, generating drastic modifications in the derivatives with each other and with the parent compound. Ring distortion reactions can be carried out by conventional chemoselective reactions using common, inexpensive, versatile, easy to handle and accessible reagents. Another useful and environmentally friendly methodology is based on the use of enzymes through chemo- and stereoselective reactions. The enzyme-mediated strategy enable to reduce the energy required and to minimize the generation of secondary products that are harmful to the environment, by using eco-friendly solvents, non-toxic and non-polluting reagents.^[3]

In this work, ring distortion reactions were performed in solidagenone (Sol), a diterpene isolated from *Solidago chilensis* Meyen, in order to obtain structural derivatives through two ring distortion reaction methodologies. Method A was based on structural rearrangements in oxidative peroxide medium using standard chemistry.^[4] Similarly, method B, is a chemoenzymatic oxidative transformation using lipase/H₂O₂ and ethyl acetate, for selectively oxidize and further rearrange furan moiety.^[5] Besides, this strategy was extended to another diterpene, isolated from the same source, Junceic Acid (JA). The structural diversity obtained in this library of compounds was evaluated by Tanimoto similarity coefficient analysis.

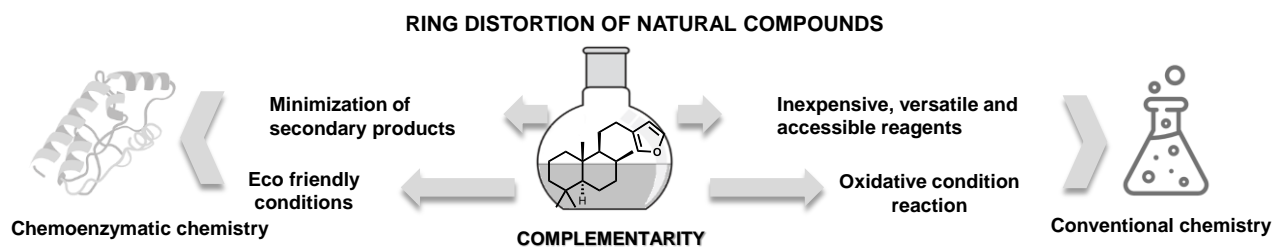


Figure 1. Conventional and chemoenzymatic oxidative derivatization of NPs.

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Oxidation of aminophenols on Ru-Au and Ru-Pd nanocatalysts supported on titanium oxide

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Oxidation of aminophenols to quinones and phenoxazinones plays a significant role in fine organic chemical synthesis, as these products exhibit biological activeness, which makes them pivotal molecules in the pharmaceutical and medicinal industries [1]. In the past, stoichiometric methods were used to synthesize these compounds. However, the use of stoichiometric oxidants often leads to low yields, poor selectivities and generates large amounts of toxic waste due to poor separation and formation of by-products [2]. In this study, titanium oxide-supported Ru-Au and Ru-Pd nanocatalysts were prepared using the microwave-polyol assisted method for the green oxidation of aminophenols to their corresponding aminoquinones and phenoxazinones. The advantages of this method include being simple, clean, short synthesis times, high products yield with an easy purification process such as simple filtration system followed by washing with water and drying processes. The synthesized nanocatalysts were characterized with spectroscopic and microscopic methods to determine their physicochemical properties. SEM (Figure 1) image of 1%Ru-1%Pd/TiO₂ showed the presence of metal nanoparticles on the TiO₂ surface (Figure 1a), and their identity was confirmed by EDX analysis. The catalysts were tested for the oxidation of 2-aminophenol and 2-amino-4-methylphenol in the aqueous media using a clean “green” oxidant, H₂O₂, at room temperature and under reflux (Figure 1b). It was observed that the catalysts’ activities and selectivities highly depend on the reaction time, type of solvent, temperature, and catalyst used. High yields of 94% (**2a**) were observed in methanol using Ru-Pd catalyst at r.t, whereas Ru-Au gave only 54%. However, Ru-Au showed better catalytic activity in nitromethane, where a yield of 68% yield (**2a**), as compared to when the reaction was carried out in methanol.

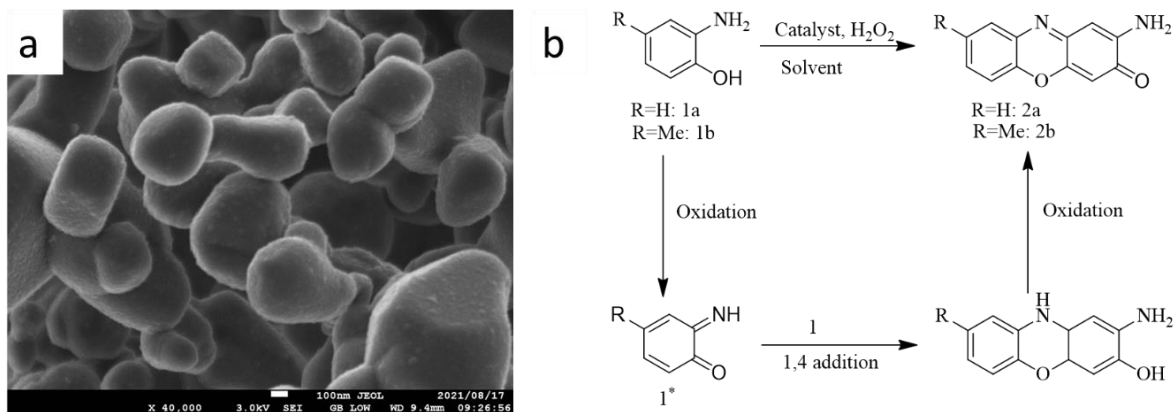


Figure 1: SEM micrograph of 1%Ru-1%Pd/TiO₂ (a) and oxidation of substituted aminophenols over noble metal catalysts in different solvents at room temperature and under reflux (b).

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Preparation of industrial primary alcohols by a one-pot hydroboration-isomerization process from waste polyolefin pyrolysis oil

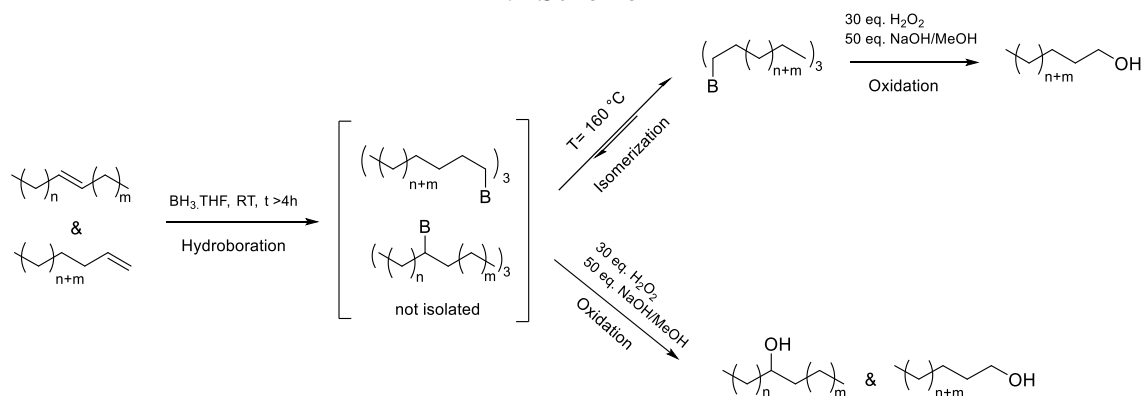
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Waste plastic comprises up to 50% of polyethylene (PE). Upon sorting, a mixed waste PE-stream is obtained, containing different types of PE, more specifically HDPE, LDPE and LLDPE. Oxygen free pyrolysis at 450°C and 1 bar, results in up to 50% of an oily substance composed of alkanes, a major portion of alkenes and a small portion of dienes. The unsaturated bonds are mostly terminal in position but internal bonds are possible. Functionalization of the double bond is an interesting concept for the valorization of said pyrolysis oil, but the mixed position of the reactive site makes this challenging as primary and secondary functional groups might result.

A one-pot hydroboration-isomerization process was elaborated yielding primary alcohols as the final product. Applying the hydroboration process proposed by Brown, a C-B bond is made by addition on the double bond (Brown and Rao 1959), (Brown and Zweifel 1960). The conditions are chosen to obtain tri-alkylboranes. In tri-alkylboranes, a shift of internal C-B bonds towards a terminal position occurs at high temperature by a successive dehydroboration-hydroboration (scheme 1) (Pazdur 2018). By applying after said shift(s) an oxidation step, primary alcohols are obtained. The process shows 95-98% conversion of both the terminal and internal alkenes to primary alcohols. Several types of WPE oil from waste PE film, LDPE, and HDPE were investigated to confirm the process. An extraction procedure to obtain pure alcohols from the mixture with alkanes was developed with a 80 % recovery. Since primary alcohol is one of the main bulk chemicals, our research provides a new efficient process for waste PE recycling as it can bring benefits for both the chemical industry and the environment.

1. Scheme 1



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Large scale synthesis of dialkyl carbonates and their application as green solvents for PVDF membranes preparation

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Dialkyl carbonates (DACs) are well-known green solvents and reagents that have been extensively investigated as safe alternatives to chlorine-based compounds, being able to replace alkyl halides and dimethyl sulfate in alkylation and carbonylation reactions as well as phosgene and its derivatives in alkoxycarbonylation ones [1]. Recently we have developed a high yielding scale-up synthesis of non-commercially available or expensive DACs via transc carbonylation reactions of an alcohol with dimethyl carbonate (DMC) promoted by the nitrogen-based organocatalyst TBD [2]. Compared to previously published works, [3] the proposed procedure has been customized for DACs large scale production (up to 100 mL of product obtained). Purification of these compounds has been achieved by fractional distillation and the exceeding reagents have been recovered and recycled. Selected DACs for this study include both symmetrical and unsymmetrical compounds, incorporating several alkyl, alkoxyalkyl, alkylamino and alkylthio functional groups. Chemical-physical properties of the new DACs have been also evaluated, as well as their water solubility. Furthermore, biodegradability and cytotoxicity tests have been carried out to investigate the effects of the different substituents on the greenness of these potential solvents and reagents. DACs application as green solvents for membrane preparation was next investigated, using non-solvent induced phase separation (NIPS) and vapor induced phase separation (VIPS) techniques, achieving both porous and plain membranes [4]. Morphology, additives effect, physical-chemical and mechanical proprieties as well as their performances in terms of water permeability and rejection were evaluated and compared to membranes obtained using commercially available cyclic carbonates (namely ethylene carbonate – EC and propylene carbonate – PC).

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Green Synthesis of an Eggshell-Derived Calcium-Terephthalate Metal-Organic Framework

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Conventionally, the Ca-Terephthalate (Ca-BDC) metal-organic framework (MOF) has been synthesized from commercial CaCO_3 [1]. This study replaced the commercial CaCO_3 reagent with waste eggshells as a source of the calcium metal centre in Ca-BDC. Evaluation of existing literature revealed that the devised procedure from eggshells is a novel concept. Furthermore, the effect of two synthetic parameters were examined to optimize the method, namely reaction temperature and time. The orthorhombic phase was exclusively obtained at 150°C , while a mixture of orthorhombic and triclinic phases was obtained below 150°C . At high temperatures, longer durations promoted Ca-BDC-tri formation, whereas at low temperatures, longer durations favoured formation of Ca-BDC-ortho. Furthermore, high dimethylformamide (DMF) and low water (H_2O) volumes hindered the synthesis of Ca-BDC. Increasing the H_2O volume above the minimum threshold that was identified provided a means to synthesize triclinic Ca-BDC purely. Therefore, waste eggshells were valorised into a high-value MOF material, thereby introducing a new method for minimizing unused food industry eggshell waste.

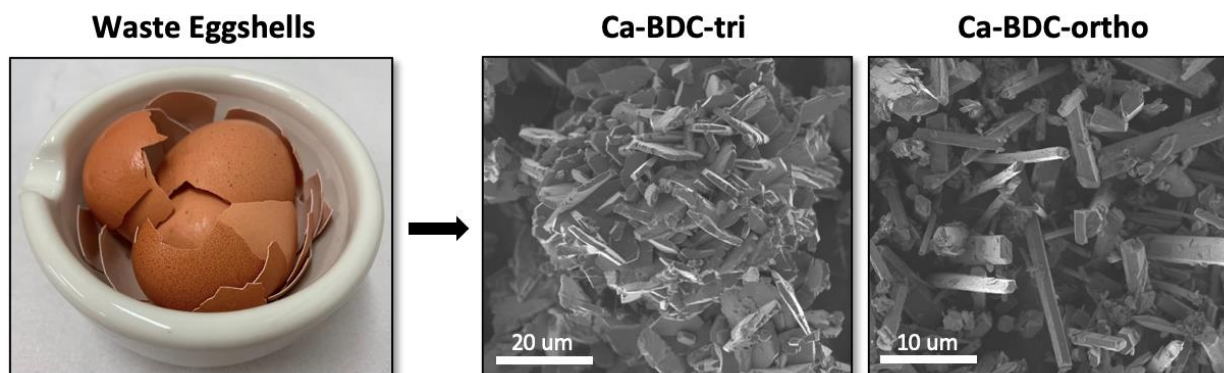


Figure 1: Synthesis of Ca-BDC MOF from waste eggshells

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Study of the Synergic Interactions of Ascorbic and Dihydroxyfumaric Acids by EPR Spectroscopy

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Antioxidant mixtures have shown atypical behavior in terms of free radical scavenging properties. For example, mixtures of antioxidants in plant extracts are more effective than individual compounds. Understanding the synergistic interactions between antioxidants is important because it can lead to the approach of effective therapies to reduce oxidative stress in the human body [1]. Using the classic colorimetric technique of the DPPH method [2] due to its high reproducibility and easy operability, we showed previously that the combination of two strong antioxidants found in grapes [3] – ascorbic acid (AA) and dihydroxyfumaric acid (DHF), has a good synergistic effect [4]. To gain a better understanding of the synergistic relationship, the study was further conducted using the EPR spectroscopy technique, able to directly detect DPPH radicals. The experiments were performed in 98% ethanol by measuring the resulting intensity of the free radical signals after 30 minutes from the addition of the mixtures of antioxidants at the concentrations found in grapes [5]: 1 – 65 (μM) for AA and for DHF. In the reaction with DPPH radical, the two antioxidants applied separately showed a good Effective Concentration (EC_{50}) of 0.24 and 0.18 (moles antioxidant/mole DPPH) for AA and DHF, respectively. Therefore, in this complementary study different concentration ratios of DHF/AA as follows: 0.5, 0.6, 0.7, 1, 1.4, 1.7, 2, have been analyzed, and it was determined that the mixtures with the ratios DHF/AA = 1.4 and 1.7 have the highest synergic effect of 1.24, which was defined by dividing the experimental value of the inhibition percentage of the mixture to the theoretical value [6]. Further, we investigated the synergic interactions of the mixture of the antioxidants at the 1.7 ratio by varying the total concentration (μM AA + μM DHF) of the reducing compounds. The FIC value of the combination AA – DHF was determined as being 0.9, which indicates a moderate synergism.

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SYNTHESIS AND INVESTIGATION OF NEW POLYCYCLIC *N*-HETEROCYCLE COMPOUNDS VIA MULTICOMPONENT REACTIONS FROM 3-ALKOXY-1*H*-PYRAZOLE-4-CARBALDEHYDES

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Multicomponent Reactions (MCRs) in which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product [1]. Multicomponent reactions are considered to be an important methodological arsenal in synthetic and medicinal chemistry. These reactions have been strategically employed in various synthetic transformations comparing to classical methods that usually involve many steps with difficult procedures. MCRs exhibit advantages such as atom economy and waste prevention, because of the reduced number of work-up, extraction and purification procedures [2]. Therefore MCRs are often considered as useful alternative to sequential multistep synthesis.

Pyrazole containing compounds are considered pharmacologically important because of many biological activities such as antioxidant, antibacterial, anticancer, anti-inflammatory and more [3,4]. This heterocyclic moiety can be found in structures of many well-known drugs for different therapeutic treatments.

In order to explore synthesis of novel pyrazole-containing by MCRs, 3-substituted 1*H*-pyrazole-4-carbaldehyde was used as a starting material. A one-stage four-component reaction was optimized and successfully applied to obtain novel 6-amino-3-methyl-4-(1-phenyl-1*H*-pyrazol-4-yl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile which was further subjected to AlCl₃ catalyzed Friedländer reaction [5]. A series of novel polycyclic 2*H*-pyrazolo[4',3':5,6]pyrano[2,3-*b*]quinoline-5-amine derivatives were obtained in fair to good yields. Also a multicomponent Hantzsch pyridine synthesis was used for the synthesis of 1*H*-pyrazol-4-yl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylates that were further oxidised to 1*H*-pyrazol-4-yl-2,6-dimethylpyridine-3,5-dicarboxylates. The structures of the synthesized compounds were confirmed by ¹H, ¹³C and ¹⁵N NMR spectroscopical investigation.

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Highly efficient separation of benzene + cyclohexane mixtures by extraction combined extractive distillation using imidazolium-based dicationic ionic liquids

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Benzene (BEN) and cyclohexane (CYH), which have very close boiling points and a binary azeotrope, are the most difficult binary components in the separation of aromatic and non-aromatic hydrocarbons. This study further explored the separation mechanism and industrial application prospects of BEN + CYH mixtures separated by a dicationic ionic liquid (DIL) $[C_5(MIM)_2][NTf_2]_2$ based on experimental research. The calculation results of the COSMO-SAC model show that selectivity and solvent capacity of the DIL are significantly improved. The effects of different anions and cations on the microstructure distribution and diffusion behavior of BEN + CYH system were investigated by quantum chemistry (QC) calculations and molecular dynamics (MD) simulations. The results indicate that the anion $[NTf_2]^-$ has low polarity, uniform charge distribution, and a dual role of hydrogen bonding and π - π bonding, the cation $[C_5(MIM)_2]^+$ has stronger interaction with BEN and higher selectivity than conventional cations. The Liquid-Liquid Extraction and Extractive Distillation (LLE-ED) process using an optimized 65% DIL + 35% H_2O mixed solution as the extractant was proposed, which solved the problem of low product purity in the LLE process and high energy consumption in the ED process. Under the best operating conditions, the purity of CYH product was 99.9%, the purity of BEN product was 99.6%, the recovery rate of BEN reached 99.9%, and the recovery rate of DIL reached 99.9%. The heat-integrated LLE-ED process reduces total annual cost by 21.6%, and reduced CO_2 emissions by 48.0%, which has broad industrial application prospects.

Keywords : Dicationic ionic liquids, Benzene + cyclohexane mixture, LLE-ED process, Quantum chemical calculation, Molecular dynamics simulation

2. EXPLOITATION OF RENEWABLE RESOURCES

Recycling of polyurethane through hydrothermal carbonization and pyrolysis process

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At the end of the life cycle of mattresses, upholstered furniture, automotive lining and cooling aggregates, mixed wastes of polyurethane (PUR) flexible and rigid foams containing textiles and other components accumulates; This waste is available in significant quantities in Europe and high-quality recycling through a chemical recycling process can make a strong contribution to the transition to a circular economy. Finding ways to recycle polyurethanes which are obviously difficult to recycle could prevent the material from becoming post-consumer waste.

The problem being solved is that conventional polyurethanes in contrary to thermoplastic materials can't be simply recycled by heating, because the material consists of polymer networks held together by strong chemical bonds that don't flow when heated. Today polyurethanes can only be downcycled into consumer materials using mechanical methods (the market is limited to a certain amount for these articles). Or Chemical recycling (methods to obtain back polyols again are also known, but the disadvantage of these methods is the high consumption of fresh polyols as process additives). Other past methods; innovative types of polyurethanes with cross-links that can be broken and reformed, allowing it to be recycled. Chemical bonds of PUR can be broken down by hydrolysis. Likewise, PUR waste can be treated via pyrolysis, however, due to the low density and agglomeration due to the low decomposition temperature of the material a direct pyrolytic conversion is currently not technically feasible.

In order to solve the existing problems, we have developed the recycling of PUR by hydrothermal carbonization (HTC) technology followed by pyrolysis. In the HTC the PUR materials are decomposed by hydrolysis and partly repolymerized to a coal like product – at the same time the volume is reduced by around 90%. In a suitable pyrolysis apparatus, the material produced in this new process can be transferred under inert conditions to fractions of oil, gas and coke. In particular, the pyrolysis oil can be used as a feed stock in petrochemical industries and can be further converted in cracking processes. The pyrolysis coke can be used as a substitution to carbon black in industry (tires, rubber and color pastes).

We carried out different physico-chemical analysis for the resulting products, such as (GCMS, IR, SEM, CHN, and Ash content). These led to a better understanding of the intermediate products produced and allow a better adaptation of the subsequent pyrolysis process.

The development of this new process is thus a key technology enabling the material recycling of mixed PUR waste.

Composite systems for photoelectrochemical reduction of CO₂

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The research aimed at designing and characterizing multicomponent composite systems capable of photoelectrochemical reduction of carbon oxide (IV) and hydrogen production under illumination of solar radiation. It investigated how copper (I) oxide (Cu₂O), a p-type semiconductor that works as a photocathode, behaves under illumination and in its absence. The surface of the electrode was modified by titanium oxide (IV), n – type semiconductor, and zeolite to improve stability of the electrode and its resistance to Cu₂O photocorrosion. Two types of electrode substrates, FTO conductive glass, and titanium sheet, were examined. Optimization of systems responsible for photoelectrochemical conversion of solar energy to alternative fuels achieved by modifying the thickness of TiO₂ or zeolite layers was also studied. The SEM technique applied in the study enabled observations of the morphology of the materials, as well as the changes on the surface after the photoelectrochemical reduction process. UV-Vis spectroscopy was used to determine the absorption spectrum of sunlight and the band gap of the material. The photoelectrochemical characteristics of obtained systems was performed in the three – electrode systems with the usage of cycling voltammetry and chronoamperometry. The same multicomponent systems have proved to be more efficient at producing hydrogen than reducing carbon dioxide. The demonstration of the activity of multicomponent systems in photoelectrochemical reactions: hydrogen production and carbon dioxide reduction can be viewed as the main contribution of the dissertation. The application of protective layers such as TiO₂ and zeolite reduces the surface recombination of generated charge carriers, stabilizes the electrodes, and increases the hydrogen production efficiency, relative to the electrode that has not been modified.

5,5'-(Oxy-bis(methylene))bis-2-furfural (OBMF) from 5-hydroxymethyl-2-furfural (HMF): a systematic study for the synthesis of a new platform molecule from renewable substances

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The continued exploitation and depletion of fossil fuels has prompted the scientific community to search for more sustainable and environmentally friendly alternatives. In the last decade, the synthesis of biomass-derived chemicals has become a priority to boost the transition from refinery to biorefinery.³ Sugars are an extremely abundant bio-resource in nature; even today, one of the most studied reactions is the synthesis of 5-hydroxymethyl-2-furfural (HMF). This compound is considered extremely important for biorefinery because of its wide range of possible applications (pharmaceutical, biofuels, polymer precursors, surfactants).⁴ However, it has been observed, during the spontaneous degenerative process of HMF, the formation of a compound that could be equally important 5,5'-[oxybis(methylene)]bis-2-furfural (OBMF).

The synthesis of OBMF is scarcely reported in the literature, only in recent years interest in this dimer of HMF has emerged for its possible applications in industry.⁵ Good yield values of OBMF are reported in the literature from HMF (Figure 1) in the presence of an acid catalyst; however, the solvents used are the most common halogenated and/or aromatic solvents, known to be toxic. The objective of this work was to find a viable synthetic route to access OBMF without having to resort to the use of such solvents and, in addition, utilize already commercially available and inexpensive acid catalysts. Through small-scale optimizations, the best solvent was found to be dimethyl carbonate;⁶ In addition, two heterogeneous acid catalysts - Purolite 269 and ferric sulfate (Fe₂(SO₄)₃) - showed excellent efficiency in promoting the HMF etherification reaction with quantitative yields (> 90%). Subsequently, a scale-up of the reaction was carried out, obtaining OBMF with an isolated yield of 73%. Given the excellent results obtained, this work can be a starting point to undertake the study of new synthetic methodologies for this molecule such as continuous flow reactions of which the literature is lacking.

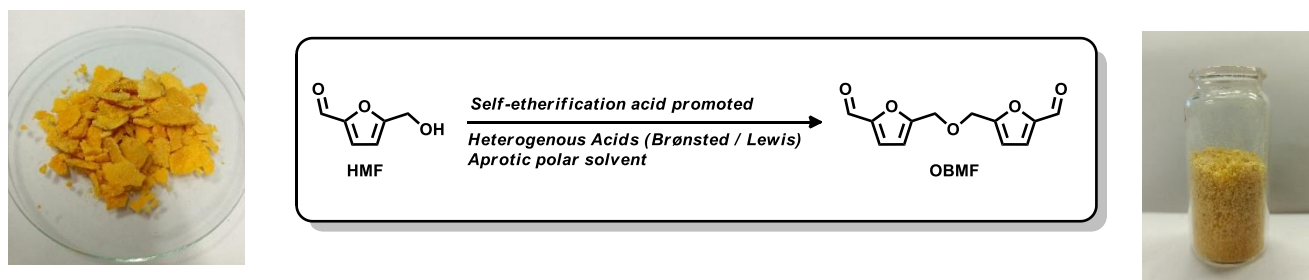


Figure 1. OBMF Synthesis from HMF.

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Sustainable Terahertz (THz) Electromagnetic Shields Based on Conductive Biochar-Nanocellulose Composites

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Terahertz (THz) communication technology has gathered humungous attention for high speed data transmission and wide bandwidth for futuristic electronic devices^[1]. Hence, electromagnetic interference associated with these THz devices has also become a major challenge and there is a strong urge to develop efficient THz shielding materials. Most of the THz shielding systems are explored with 2D materials such as Graphene, MXene and/or their analogues but their fabrication and processing steps are not environmentally benign and very expensive^{[2][3]}. In this work, we made use of plant sourced cellulose nanofibers (CNF) and biochar from agricultural residues to fabricate highly conductive aerogels and nanopapers to address this upcoming problem. These biobased nanocomposites showcase tremendous potential for absorbing THz radiations and is considered as a fully sustainable solution to screen THz radiations for next generation high frequency electronic components.

Keywords

Cellulose Nanofibers (CNF), Conductive Biochar, Biomass Valorization, Aerogels, Nanopapers, THz Shielding.

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SAPONINS FROM THE RIND OF *Napoleonaea imperialis* P. BEAUV

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Napoleonaea imperialis P. Beauv (family Lecythidaceae) commonly called Napoleon's hat is a medicinal plant found in South-Eastern Nigeria. The rind was separated from the seed and macerated using methanol. The crude methanol extract was partitioned to yield n-hexane fraction (7.4%), dichloromethane fraction (23.7%) and methanol fraction (68.7%). The dichloromethane fraction was chromatographed and further purified to give compounds whose structures were elucidated using one-dimension and two-dimension nuclear magnetic resonance (NMR) experiments. The isolated compounds were characterized as 3-O-[D-glucopyranosyl(1→2)-D-glucopyranosyl]-21,28-diangeloyloxy-24-hydroxy-olean-11,13(18)-diene and glycosylated stigmasterol.

Microalgae *Chlamydomonas reinhardtii* extracts and their antimicrobial activity

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Microalgae are involved in a variety of bioactive metabolites. They manifest a great variety of biological activities. The increasing demand for drugs able to cure new diseases resistant to commonly used medicines arouses interest in unconventional new sources of bioactive natural compounds. Recent scientific investigations have revealed that microalgae compounds exhibit various beneficial biological effects such as anti-inflammatory, antimicrobial, anticancer, anti-HIV, antihypertensive, antidiabetic, and several more medicinal effects. Thus, it is of growing importance to shed light on the pharmaceutical activities of bioactive components from microalgae and to maximize their recovery from microalgal biomass. Concerning this latter point, in general, the factors that influence the extraction yield of the biological compounds from microalgae depend on the extraction method, the pretreatment of biomass, and the nature solvent used, which is the most critical factor. Organic solvents are commonly used methanol, ethanol, acetone, and ethylene glycol and their aqueous solutions. However, due to the varied physical and chemical natures of the components present in microalgae biomass, different solvents are required to optimally exploit the potentialities of the compounds produced by given microalgae. Furthermore, sustainable processes are desirable, and green solvents need to be used to replace conventional ones (Alfieri et al., 2022).

The focus of the present study was to optimize the extractions with green organic solvents. For the extractions, the freeze-dried biomass of a strain of *Chlamydomonas* was used, and in each case after adding the various solvents, the biomass was sonicated to promote cell rupture, favoring extraction. The green solvents used for extraction were methanol, dimethyl carbonate, ethyl methyl ketone, and cyclopentyl methyl ether (Alfieri et al., 2022). Furthermore, green organic solvent extractions were compared with an extraction technique using a hydroalcoholic solution and subsequent extractions with chloroform, hexane, and ethyl acetate (Yu et al., 2019). The best extraction yields were obtained with methanol and cyclopentyl methyl ether (21% and 19% weight of extract / initial dry biomass weight, respectively).

After removing all the solvent from the extract, the latter was solubilized in an aqueous solution containing DMSO and TWEEN to improve the diffusion of the extracted molecules on the agar plate. Subsequently, the extracts were tested against the model microorganism *Bacillus megaterium* using the agar well diffusion method. All the extracts obtained with green solvents showed antimicrobial activity. In particular, the best results were obtained with Ethyl methyl ketone and cyclopentyl methyl ether, which showed zones of inhibition of 2.1 cm and 2.2 cm respectively.

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Single-step production of green butadiene over bimetallic silica-supported catalysts

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Since the 1910s, studies have been conducted on renewable raw materials such as substitutes for petrochemical derivatives in the synthesis of industrial products. One of these products, the 1,3-butadiene, is an important chemical intermediate and monomer for some polymers and synthetic rubbers. This olefin is mainly produced through naphtha steam cracking as a byproduct of ethylene production. Oil price fluctuations, reduced availability of natural gas and naphtha, and the discovery of large shale gas reserves in the United States make it necessary to look for alternative routes to produce 1,3-butadiene [1,2]. In Brazil, ethanol matrices have been used to develop green technologies due to their big offer, renewable configuration, low cost, Proalcool incentives (a former national government program), and various applications in the energy and chemical sectors.

This work aims to study the synthesis of 1,3-butadiene from ethanol in a single step to propose a process and optimize the reaction conditions. To this end, we used a bench-scale unit with a fixed bed catalytic microreactor, including an analysis GC/MS. Based on the results obtained, process simulations on Aspen Hysys® were performed, including reaction and separation steps. The catalyst formulations were prepared in this work by adding 1,5% - 0,5% molar bimetallic promoters over amorphous silica using the wet kneading method.

The bimetallic catalysts showed high selectivity to ethene, independent of the formulation used. The samples with 1,5% molar Co - 0,5% molar Zn and 1,5% molar Ni - 0,5% molar Zn obtained a higher selectivity to 1,3-butadiene (between 98% molar of ethanol reacted), indicating a predominance of acid sites in the catalyst, which directs the reaction to the formation of unwanted byproducts. The zinc-copper formulations presented the most promising results, with ethanol conversion greater than 99% molar and about 65.19% molar formation of 1,3-butadiene and acetaldehyde. Although the selectivity to 1,3-butadiene was not high, these samples were selective in forming acetaldehyde, an intermediate product of 1,3-butadiene production. This last group of catalysts is promising, and the optimized reaction conditions on Aspen Hysys® showed 94% of green butadiene obtained.

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Semi-Transparent Cellulose Nanofiber from Cellulose Acetate/Lignin Nanofibers

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This study reports the first attempt for production of semi-transparent electrospun cellulose nanofibers through a facile processing method. Semi-transparent cellulose nanofibers were produced by deacetylation and deligninification of cellulose acetate (CA)/lignin(L) nanofibers fabricated through electrospinning using aqueous dispersion of lignin and cellulose acetate. The defect-free nanofibers were achieved with using 5 wt% L and 15 wt% CA. Deacetylation and deligninification of CA/L nanofibers was done by NaOH solution led to the foldable, high-strength and optically semi-transparent electrospun cellulose nanofibers.

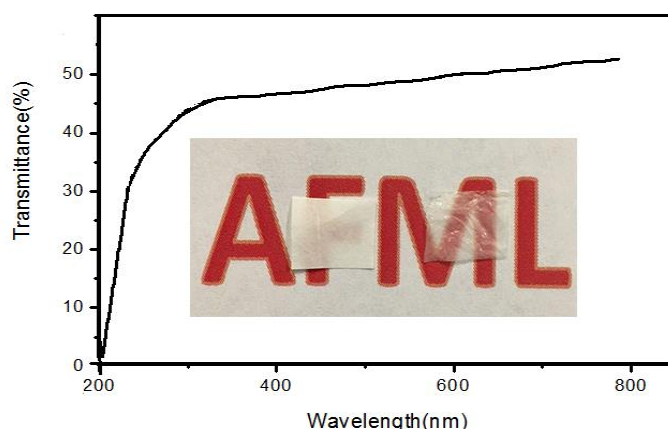


Figure 1. UV-Vis transmittance of nanofibers prepared from deligninification and deacetylation of CA/L nanofibers.

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Preparation of nanobiocomposites based on halloysite nanotubes-zein and evaluation of their performance for thin film microextraction

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In this work, a biocompatible sorbent based on halloysite nanotubes-zein bionanocomposite for direct-immersion thin film microextraction (DI-TFME) is introduced. Zein as a biodegradable, low cost and accessible polymer was used to prepare a flexible thin film with the possession of different interactions and good adsorption capacity [1]. To improve the mechanical and chemical resistance of the film [2], halloysite nanotubes were combined with zein to prepare the thin film sorbent. The film was used for TFME of 16 pesticides from different chemical classes, including organochlorines and organophosphates followed by gas chromatography with electron capture detector (GC-ECD). To achieve the maximum efficiency and sensitivity, effective parameters such as the amount of halloysite nanotubes in bionanocomposite, type and volume of desorption solvent and desorption and extraction times were investigated and optimized. The linear dynamic range of the method was in the range of 0.1–300 $\mu\text{g L}^{-1}$. The limits of detection and limits of quantification of the method were in the range of 0.01–0.04 $\mu\text{g L}^{-1}$ and 0.02–0.12 $\mu\text{g L}^{-1}$, respectively. The relative standard deviations for three replicates at the concentration levels of 5 and 50 $\mu\text{g L}^{-1}$ were in the range of 3–12%. The method was validated for the TFME of pesticide residues in honey samples and recoveries for the spiked samples at two concentration levels of 5 and 50 $\mu\text{g L}^{-1}$ were found to be in the range of 79–118%. The analytical results of the present method were comparable with some relevant methods currently used for the determination of pesticide residues. Besides, the prepared sorbent was environmentally friendly, easy to prepare, and inexpensive.

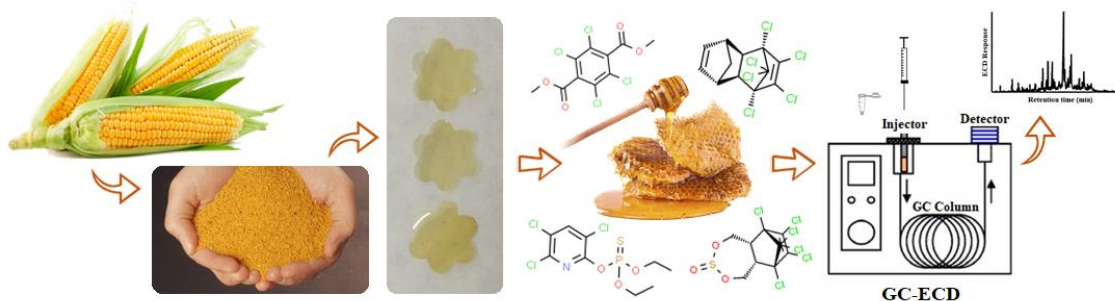


Figure 1. Graphical abstract

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New insights into CO₂ suppression in biomass oxidation to formic acid catalyzed by vanadium-substituted heteropolyacids

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Formic acid (FA) is widely used in the preparation of various chemicals, applied to fuel cells, and is considered to be a good hydrogen storage material. For the needs of sustainable development, it is necessary to use renewable resources rather than fossil resources to produce FA. Catalytic O₂ oxidation of biomass with a vanadium-substituted heteropolyacid as catalyst is a promising method for the preparation of FA. However, as the reaction process is often accompanied by the production of CO₂, the yield of FA is limited. Herein, the catalytic O₂ oxidation of glucose using H₅PV₂Mo₁₀O₄₀ as catalyst was divided into two steps: glucose oxidation and catalyst re-oxidation. The rate relationship between them and the product distribution were studied by kinetic experiments and control experiments. The rate of glucose oxidation increases faster than that of catalyst re-oxidation with increasing temperature. A rate matching relationship is proposed to minimize the over-oxidation and hydrolysis. On the other hand, the addition of some low carbon alcohols or dimethyl sulfoxide can suppress CO₂ and increase the yield of FA markedly. With the addition of isopropanol, the yield of FA and its ester increases from 51.9% to 92.2% for glucose. Mechanism studies disclose that the high selectivity of FA are attributed to the scavenging of hydroxyl radical from the re-oxidation of HPA-*n*. Hydroxyl radical scavengers prevent aldehyde group from being oxidized to carboxy group as the precursor of CO₂. The formation of hydroxyl radical is indicated both by catalyst re-oxidation experiments and ESR experiment. Besides, the effect of isopropanol dosage and different biomass as substrate on CO₂ suppression is studied.

Keywords: Glucose, Catalytic oxidation, Formic acid, CO₂ suppression, H₅PV₂Mo₁₀O₄₀

**Study of the Functional Groups Associated with the Corrosion
Inhibition of Stainless Steel Arch Bar in Acidic Medium by Khaya
Grandifolia Gum Exudate**

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The corrosion inhibition of stainless steel arch bar (an implant used for maxillo-mandibular fixation in dentistry) by Khaya grandifolia gum exudates in 1.00×10^{-4} mol dm⁻³ HCl solution and pH of 4.0 was studied using weight loss method (gravimetric analysis). The corrosion rate decreased in the presence of the gum exudate while the inhibition efficiency was observed to increase with an increase in the concentration of the gum exudate. Variation of the inhibition efficiency with time showed a decreasing trend, FTIR analysis of the gum exudate (crude and in HCl) showed the presence of some functional groups that might have been used in adsorbing the inhibitor unto the surface of the metal. The observed functional groups included OH stretch, C=C, C=N, or C=O functional groups and C-C, C-N, and CO due to carboxylic acid stretching or alcohol bonds in the gum. Surface analysis showed remarkable improvement on the surface, in the presence of the inhibitor than in its absence.

Pretreatment of seawater by ceramic membranes Prepared by alternatives raw materials

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Algeria is one of the countries that suffer from water stress due to the lack of water resources. This is why the use of desalination reverse osmosis (RO) is now an effective solution for the supply of drinking water, which currently presents 17% of national water production capacity and will reach 35% by 2030. A very high SDI and turbidity characterize seawater, which can damage the membrane (RO) by irreversible fouling, it is for this reason that pretreatment is essential before desalination by reverse osmosis system. There are therefore two methods for the pretreatment of seawater: conventional methods and membrane methods (ceramic membranes). A membrane is semi-permeable filters that separate salts and other constituents dissolved in water and water itself. In this work we try to draw attention to alternative raw materials that we use for the preparation of membranes such as natural geomaterials, agricultural wastes, industrial wastes and animal bones, which are very abundant, improve the key performance of the ceramic membrane and reduce energy costs due to their low sintering temperature. The use of these alternative raw materials allows not only to preserve our environment but also to replace silica, alumina and titanium dioxide, which are very expensive and are characterized by a high sintering temperature. Below we present a summary table to this type of raw materials.

In this research work, we will present the preparation of ceramic membranes for the Mediterranean seawater pretreatment in the Algerian coastal region (Bouïsmail Town) using local and alternative raw materials. The influence of various parameters on the membrane performance such as a raw material composition, sintering temperature on membrane porosity, pore volume and mechanical strength will be also given and discussed.

Table 1. Summary table to alternative raw materials [1].

Natural Materials	Agro Waste	Industrial Waste	Waste Animals Bones
Cly (kaolin,bauxite,bentonite Sand, natural zeolite...	Rice husk ash Sugarcane bagasse ash Coffee bagasse ash.	Fly ash, Aluminum dross.	Waste cow bones Waste fish bones Waste pig bones

Keywords: Ceramic membranes, pretreatment, alternative raw materials.

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Biodiesel production using cellulose-supported calcium hydroxide heterogeneous catalyst synthesized from phosphate rock.

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Calcined phosphate rock was used as a precursor material for calcium hydroxide catalyst. Coprecipitation method was used to support the catalyst on cellulose nanocrystals. One factor at a time experimental design was used to study the effects of methanol to oil ratio, catalyst concentration, reaction time, and reaction temperature on biodiesel yield. The optimum working conditions for the supported catalyst that gave a maximum yield of 96%wt were methanol to oil ratio 1:8, reaction temperature 60⁰c, catalyst concentration 4.0wt% and reaction time 1hr. Scanning electron microscopy and Fourier transform infrared spectroscopy were used to check the loading of the catalyst on cellulose nanocrystals. The results revealed the successful loading of the catalyst onto the support material. Biodiesel samples were analysed in a Gas Chromatography to confirm the conversion of the raw waste oil into biodiesel. The physical and chemical properties of biodiesel were checked and compared to the ASTM D6751 international standards and were found to be within the expected ranges.

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The HMF, the key to green chemistry through the circular economy

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The circular economy is essential for the sustainability of our planet and is strongly linked to green chemistry and its principles, where not only the fact of using waste is important, but also the possibility of working at low or moderate temperatures, using green solvents and catalysts or working with systems capable of obtaining products with a high-added value in the most efficient and safe way possible.

In this work, two main objectives are studied: firstly, the use of lignocellulosic biomass residues to obtain its main components separately (cellulose, hemicellulose and lignin) after treatment with a green solvent. Secondly, use cellulose to obtain a very important product in the petrochemical industry, 5-Hydroxymethylfurfural (HMF), which is a precursor platform molecule for many high-added value compounds such as biofuels, solvents, resins, adhesives, coatings, additives and even bioplastics.

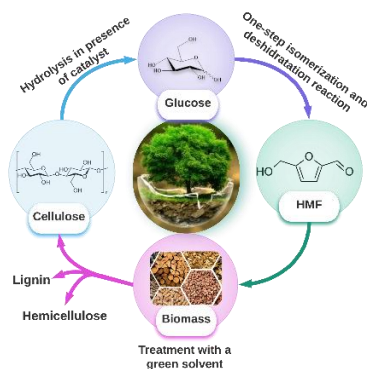


Figure 2. Scheme with the main objectives of the work applying principles of green chemistry.

As shown in the following scheme, from lignocellulosic biomass a treatment will be carried out with green solvents that can be reused (ionic liquids¹ or inorganic salt hydrates²). After that, cellulose is recovered and will be used in acid hydrolysis to obtain glucose³, which will come into contact with a heterogeneous catalyst designed with two different acid centers (Lewis and Brønsted) based in Metal Organic Frameworks combined with Polyoxometalates to obtain HMF in one-step⁴, to isomerize glucose to fructose and subsequently for dehydration of fructose to HMF. This catalyst is recovered and reused in the system again.

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COMPARATIVE STUDY OF THREE ECO-FRIENDLY GREEN MATERIALS FOR INHIBITION AND CONTROL OF MILD STEEL CORROSION

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The green materials used for this study were: *Costus Afer* (COA), *Uvaria Chamae* (UVC), and *Xylopiia Aethiopia* (XYA). The choice of materials were informed by the rich iron content shown by the leaves during metals analysis and their tendencies to act as oxygen scavengers in a corrosion prone system. The inhibitive action of the methanol extracts of these leaves on the corrosion of mild steel in 2.5 M HCl solutions with inhibitor concentrations of 0.5 g/L, 1.0 g/L, 2.0 g/L and 4.0 g/L, at the temperatures of 30°C and 60°C was studied using gravimetric (weight loss) and gasometric (hydrogen evolution) techniques to determine their inhibition efficiencies as well as to characterize the mechanism of inhibition of these three green inhibitors. The gravimetric technique was done for 5 days (120 Hours). Results indicate that the leave extracts inhibit the corrosion process in mild steel efficiently without any significant environmental hazard. COA, UVC and XYA extracts showed inhibition efficiency of (83.7, 84.6 and 87.0) and (85.0, 62.5 and 76.1) for gravimetric (weight loss) and gasometric analysis respectively. The Inhibition efficiency was found to increase with an increase in the extract concentration and decrease with an increase in time(days) and temperature. The inhibition efficiencies followed the trend XYA>UVC>COA and COA>XYA>UVC in gravimetric and gasometric analysis respectively. Thermodynamic considerations revealed that the activation energy, E_a increased in the presence of the plant extracts. The kinetic data confirmed the reaction process to be first order. Adsorption of the plant extracts on mild steel surface is an exothermic process and spontaneous as deduced by mostly negative Q_{ads} mean values of -7.40 KJ/mol, -2.14 KJ/mol and -32.18 KJ/mol for COA, UVC and XYA and negative ΔG_{ads} values of -9.28 KJ/mol and -12. 0 KJ/mol for COA, -9.46 KJ/mol and -11.23 KJ/mol for UVC and -7.73 KJ/mol and 6.29 KJ/mol for XYA at 30°C and 60°C respectively. The mechanism of adsorption proposed for the plant extract on the mild steel surface is physical adsorption. Experimental data obtained fit the Langmuir adsorption isotherm.

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HEALTH RISK ASSESSMENT OF TRACE METALS IN VEGETABLES AND SOIL WITHIN THE VICINITY OF FIRST TECHNICAL UNIVERSITY, IBADAN, OYO STATE

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The amounts of heavy metals (Ni, Zn, Pb, Cu, and Cd) in the soil at 0-15cm and 15-30cm, as well as vegetable samples *Talinum triangulare*, *Corchorus olitorius*, and *Celosia argentea* grown at First Technical University Ibadan, Oyo State, were determined in this study. This was done to measure the degree of heavy metal contamination in soil and plants caused by human activities like industrialisation. It also revealed the health concerns posed by metals found in soil and plants.

A total of six (6) soil samples and twelve (12) vegetables samples were analysed. The samples were collected and digested with nitric acid (HNO₃) and Perchloric acid (HClO₄), Hydrofluoric acid (HF) using thermostatically hot plate. The worked-up samples were run on the Buck Scientific Atomic Absorption Spectrophotometry (AAS) 200 series. The results showed that the concentrations of the metals in soils sample at different location (0-15cm and 15-30cm) ranged from Zn (7.78 ± 0.002 to 9.85 ± 0.002 µg/g), Pb (0.65 ± 0.002 to 0.96 ± 0.002 µg/g), Cu (0.13 ± 0.001 to 6.26 ± 0.38 µg/g), Ni (7.93 ± 0.002 to 10.100 ± 0.002 µg/g), Cd (0.05 ± 0.001 to 0.56 ± 0.002 µg/g) the values were lower than the standard maximum permissible level recommended by World Health Organisation of Zn, Ni, Cu, Cd and Pb as 300, 50, 100, 3 and 100 respectively.

Also, the concentrations of the metals in vegetable sample at different part (leaf, stem and root) and location is in the order of Ni > Zn > Cu > Pb > Cd which ranges from Zn (0.08 ± 0.001 to 11.70 ± 0.002 µg/g), Pb (0.50 ± 0.002 to 1.038 ± 0.002 µg/g), Cu (0.25 ± 0.001 to 5.83 ± 0.18 µg/g), Ni (5.30 ± 0.001 to 12.30 ± 0.002 µg/g), Cd (0.05 ± 0.001 to 0.33 ± 0.001 µg/g) the values Ni, Zn, Cu were below the standard maximum permissible level recommended by World Health Organisation of Zn, Ni, Cu, Cd and Pb as 99.4, 67.0, 73.0, 0.1 and 0.3 respectively while Pb and Cd were above the maximum permissible level of heavy metal in vegetable.

The total hazard quotient (THQ) and hazard index (HI) values for both adult and kid were over the permitted range, suggesting that vegetable consumption poses a carcinogenic risk to residents. The health risks for metals in soil that are CDI carcinogenic (x 10⁶) and CDI non-carcinogenic (x 10⁶) for Zn, Ni, Cu, Cd, and Pb were found to be lower than the permissible level in this study. In terms of discussing preventative ways for minimizing heavy metal pollution in soil and plants, the present study will be incredibly valuable to both children and adults.

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Isolation and Characterization of Starch from *Citrus sinensis* Albedo as Bioplastics

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Plastics has proven to be a useful component of our living, with uses ranging from domestic and industrial applications, however, they also contribute dominantly to environmental pollution and climate changes. Fruit wastes on the other also attributed to pollution, as a way of solving these two undeniable challenges, this project isolates and characterise starch from citrus sinensis albedo as bioplastic. The isolation of starch was carried out using the centrifuge and leaching was done with hydrogen peroxide. Proximate analysis indicates the presence of carbohydrates, while the FTIR characterization of the albedo, and isolate, both bleached and unbleached indicated multiple OH groups in the unbleached with are absent in the bleached starch due to the activity of the Hydrogen peroxide. The onset of crystallisation was observed with the XRD with the presence of lumps in the SEM microgram which shows the possibility for modifications and perhaps, compounding with other materials to form a biocomposite where properties can be worked upon. This project shows the usability of the starch from *citrus sinensis* as a viable source of bioplastic for domestic and industrial uses.

Table 1: Result of Proximate Analysis

Sample ID	Crude Protein (%)	Crude Fat (%)	Crude Fibre (%)	Total Ash (%)	Moisture Content (%)	Carbon-hydrate Content (%)	Dry Matter (%)
RO	3.39	0.64	1.75	1.24	12.49	80.49	87.51

RO: Raw Orange Albedo.

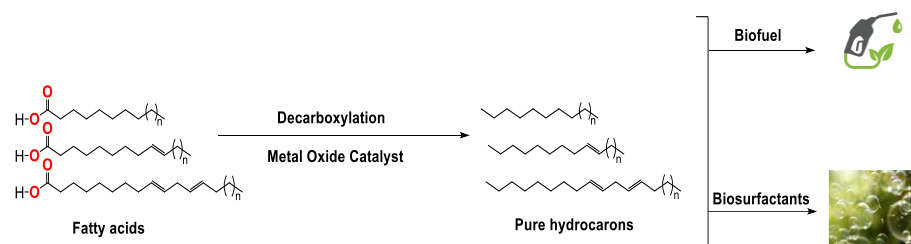
Fatty acid conversion to value-added chemicals and fuel additives by La-promoted Ni/SBA-15 catalyst

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The replacement of fossil-fuel with renewable and sustainable sources of energy and chemicals is needed. Lipid-based biomass has garnered considerable interest owing to its abundance, affordability, low toxicity, and biodegradable nature.¹ Ketonic decarboxylation of lipids is an essential tool in producing long carbon chains (C18-C36) that are similar to fossil-fuel-derived hydrocarbons². Among the commonly used transition metals, nickel is readily available and has a high hydrogenolysis ability.³ However, limitations such as the understanding of the reaction mechanism, the use of molecular hydrogen and upscaling for industrial applications is still prevalent.⁴ In this work, nickel supported on silica nanoparticles was synthesised and promoted with lanthanum as a catalyst in the deoxygenation of fatty acids to improve the reaction activity and selectivity. Catalytic deoxygenation of fatty acids to form bio-hydrocarbons was carried out under moderated conditions without using molecular hydrogen.



Scheme 1: Catalytic deoxygenation of triglycerides to form bio-hydrocarbons.

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Bioplastics that grow on trees

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Currently, we find ourselves in a world economy turning towards sustainability, and with plastic in the crosshairs of environmental campaigns. Thus, bioplastics are the sustainable solution of the future.

The search for new energy sources as substitutes for fossil fuels is necessary because these are finite resource. A new alternative is the use of lignocellulosic biomass because it offers a high potential for the production of value-added compounds in the framework of a circular economy. In addition, lignocellulosic biomass represents an important source of raw materials without compromising the food supply.

In this work, we will focus on the fractionation of biomass by catalyzed bi-phasic organosolv process [1] because it has a highly compacted structure made up of cellulose, hemicellulose and lignin. The next step after pretreatment is carbohydrate hydrolysis to generate a sugar-rich stream that is used as a platform for the production of a large array of bioproducts.

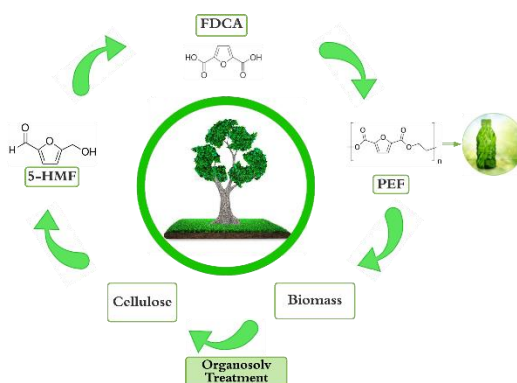


Figure 1. Scheme to obtain plastics from biomass

In Figure 1 we can distinguish 5-Hydroxymethylfurfural (5-HMF), a platform chemical product that is produced by dehydrating sugars, which in turn is obtained from the conversion of cellulose [2]. The importance of obtaining 5-HMF lies in the fact that this compound can be oxidized to FDCA, which is a precursor of PEF, a polymer that is the current alternative to plastics obtained from PET.

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New bio-based sustainable polymers and polymer composites based on methacrylate derivatives of furfural, solketal and lactic acid

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Monomers derived from renewable sources are of great interest to drive sustainable polymer chemistry [1,2,3,4]. Herein, bio-based furfural, glycerol, and lactic acid were used as building blocks to prepare methacrylate monomers *via* simple transesterification reactions in high yield and purity. The monomers were polymerized and co-polymerized by employing a free radical solution polymerization technique using 1,1-azobis cyclohexanecarbonitrile (ABCN) initiator. The resultant new co-polymers (P(FAMA-co-SoMA), P(FAMA-co-LAMA), and P(SoMA-co-LAMA)) were obtained in high yields and proved to have sizeable molecular weights (M_w from 2540 – 29395 gmol^{-1} and M_n from 2194 – 7463 gmol^{-1}). Thermogravimetric analysis and differential scanning calorimetry (DSC) measurements on these polymers revealed good thermal properties (thermal stability ranging between 125 °C and 155 °C) with some crystalline regions identified by DCS and PXRD. The polymers were reinforced using cellulose triacetate and polysulfone to give new polymer composites (Psf/PFAMA, Psf/PFAMA-co-SoMA, Psf/PSoMA, CTA/PFAMA, CTA/PFAMA-co-SoMA, CTA/PSoMA), which were amorphous and degraded hydrolytically (in acidic and basic aqueous solutions) by up to 10% in just 24 hours. The polymer composites were fashioned into thin films and membranes and applied preliminarily as coatings and water filtration membranes.[5]

Keywords: *Bio-based, Furfural, Glycerol, Lactic acid, Polyacrylate, Renewable, Sustainable.*

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Characterization of food waste and sugar wastewater for biogas production

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Energy accessibility and waste management are some of the most significant challenges African countries face, including South Africa ^[1]. On the other hand, waste can be used as a renewable resource to produce energy ^[2]. This resource is one of the sustainable, old, and viable routes to help many developing countries manage massive amounts of the waste left unattended in landfills and discharged into water streams and oceans ^[3]. This waste emanates in either liquid or solid form and negatively impacts the environment and, consequently, life in such an environment, i.e., human and animal lives ^[4]. Among many ways of solving this waste issue is using it as a resource for producing valuable products such as biogas, biofuels, etc., which contribute to the circular economy ^[5]. Also, this is in line with UN's Sustainable Development Goals 5, 7, 8, 9, and 13. Biogas can be produced from many substrates including organic solid waste, wastewater/ effluent etc. as substrates in a process called biodigestion. Research has shown that digestion of a single substrate produces less biogas than a co-digestion of two or more substrates. In this regard, the current research characterizes food waste and sugar wastewater for use as co-substrates for biogas production.

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Performance Evaluation of Glutaraldehyde-Modified Polyphenolic Resin as Oilfield Scale Inhibitors

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Oilfield operations being a complex one, involves series of professional operations and application of sophisticated equipment and chemicals. Some of these operations risk the occurrence of scale deposition, thus inhibitors are used to mitigate scale formation during these operations. In this experimental study, a biomass-derived glutaraldehyde-modified derivative of Red Onion Skin Extract (ROSE) was used in the formulation of scale inhibitors. The glutaraldehyde-ROSE derivative and ROSE were subjected to Fourier Transform-InfraRed spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Their inhibition efficiency was experimentally evaluated using the static jar test, at inhibitor concentration of 20ppm - 100 ppm, temperature of 71 °C and 90 °C, and a contact time of 4 and 24 hrs, under static conditions. Th synthetic brine used for the study was formulated according to the NAICE method. The compatibility of brine with the developed scale inhibitors was evaluated at ambient; 25 °C, and 90 °C temperature, immediately and after 24 hrs at 25 °C, and 15 min at 90 °C respectively. The data obtained revealed that no precipitation took place at the scale inhibitor concentration and temperature studied, which confirms it is compatible with the brine. The thermal stability of the prepared inhibitors was evaluated at 130 °C, the result obtained before and after exposure indicate that they are thermally stable. The scale mitigation potential of the glutaraldehyde-modified polyphenolic resins on calcium sulphate, calcium carbonate and barium sulphate scale deposits, revealed that they had good inhibition efficiency. Their scale inhibition performance was as follows: calcium sulphate scale; showed the highest inhibition efficiency of 67 % at 100 ppm, followed by calcium carbonate scale, with an inhibition efficiency of 56 % at 100 ppm. Barium sulphate scale, however, showed a high inhibition efficiency of 88 % at 80 ppm. These results show that the prepared inhibitor can efficiently inhibit formation of CaSO₄ and BaSO₄ scales, however, increased concentration maybe required to inhibit the calcium carbonate scale. These inhibitors have good scale inhibition potential and could be used as a sustainable substitute for oilfield scale inhibition.

Keywords: Red Onion Skin Extract (ROSE), Scale Inhibitor, Quercetin, Bio-based Resins, Polyphenolics

Conversion of hemicellulosic biomass into furan derivatives

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Fossil fuels are currently the major source of chemicals and fuels, however, global issues such as the increase in prices of these refined fuels, their dwindling supply and climate changes due to the release of greenhouse gases into the atmosphere have led to the search for cleaner and sustainable energy sources.^{1,2} Biomass is the most sustainable organic carbon source of energy that can be valorized into useful compounds, with Africa being the largest producer.³ The use of ionic liquids (ILs) have gained attention when it comes to the conversion of biomass due to their unique characteristics and advantages over the mineral acids that is being used industrially.⁴ However, due to the high cost in synthesizing these solvents their global application have become very limited. The acidic character of the ionic liquids can be Lewis, Brønsted or a combination of both.⁵ Furthermore, there are several reports where metal chlorides used as co-catalysts together with ILs improved upon the conversion of biomass.⁶ Ionic liquids containing nitrogen-based cations have been explored extensively especially in the conversion of biomass. There is just a few of phosphonium based ionic liquids that have been studied so far, therefore this represents a promising area of research that should be investigated.⁷ We therefore report on the synthesis of new, simple and cost effective phosphonium and imidazolium ionic liquids containing both Brønsted and Lewis acid sites for the dissolution of plant biomass, in order to release their individual components (hemicellulose, cellulose and lignin). The hemicellulose fraction, which contains pentoses (mainly xylose) undergoes a sequence of acid-catalyzed hydrolysis → dehydration reaction steps to produce furfural (FFR) and other furan derivatives which can further be valorised to other useful chemicals and fuels.^{8,9}



Figure 1: Conversion of biomass with ionic liquids into useful compounds

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Formulation and Characterization of the Natural Fiber/Polymer Composites from Waste Pineapple Leaf Fibers

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Many varieties of agricultural residues/waste (e.g. pineapple leaf fibres (PALFs)) are produced all over South Africa (SA) in massive quantities. Agricultural waste has been burned in the fields by South African farmers as an easy and cheap way to remove stalks after harvests. However, this practice significantly contributes to SA's carbon dioxide emissions and health risks associated with the thick mists it produces. The PALFs are renewable biomass resources, and they can be used to make new marketable materials, but their full potential has not yet been realized. Since PALFs are rich in cellulose, hemicellulose, and other carbohydrates, PALFs were found to be a potential source for cellulose nanofibers (CNFs) that can be functionalised and applied to the agricultural water saving materials. The aim of this study was to isolate, characterize and functionalize CNFs from raw PALFs by using alkali hydrolysis method. Polybutylene succinate (PBS) /PALF Composites. The composites were prepared with the fibre content ranging from 0 – 20 wt.%. The blends of PBS polymer and PALF were mixed by an internal batch mixer that is operated at a temperature of 120 °C with a speed of 40 rpm. The morphological and structural properties of the extracted PALFs/polymer composites were evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Thermogravimetric Analysis (TGA). FTIR confirmed that alkaline treatment and bleaching removed most of the hemicellulose and lignin components present in the PALF fibres and the intensity of the peak decreases with the increasing amount of PALF in the composites. XRD studies revealed that the incorporation of PALF disrupts the crystallinity of the PBS polymer chains. Thermal analyses shown that the developed composites exhibit improved thermal properties. The water absorption experiments were performed to evaluate the resistance of the composites to moisture and the percentages of water absorption are below 30 % reflecting that all composites have good water resistance.

In conclusion, the PALF/PBS composites isolated have potential to be applied in agricultural water saving materials (plastic mulching films).

Table 1. Formulations of the PBS/PALF Composites.

Sample Name	Mass of PBS (g)	Mass of PALF (g)
PBS-PALF-0	53.11	0.00
PBS-PALF-5	49.33	2.60
PBS-PALF-10	46.73	5.19
PBS-PALF-15	44.13	7.79
PBS-PALF-20	41.54	10.38

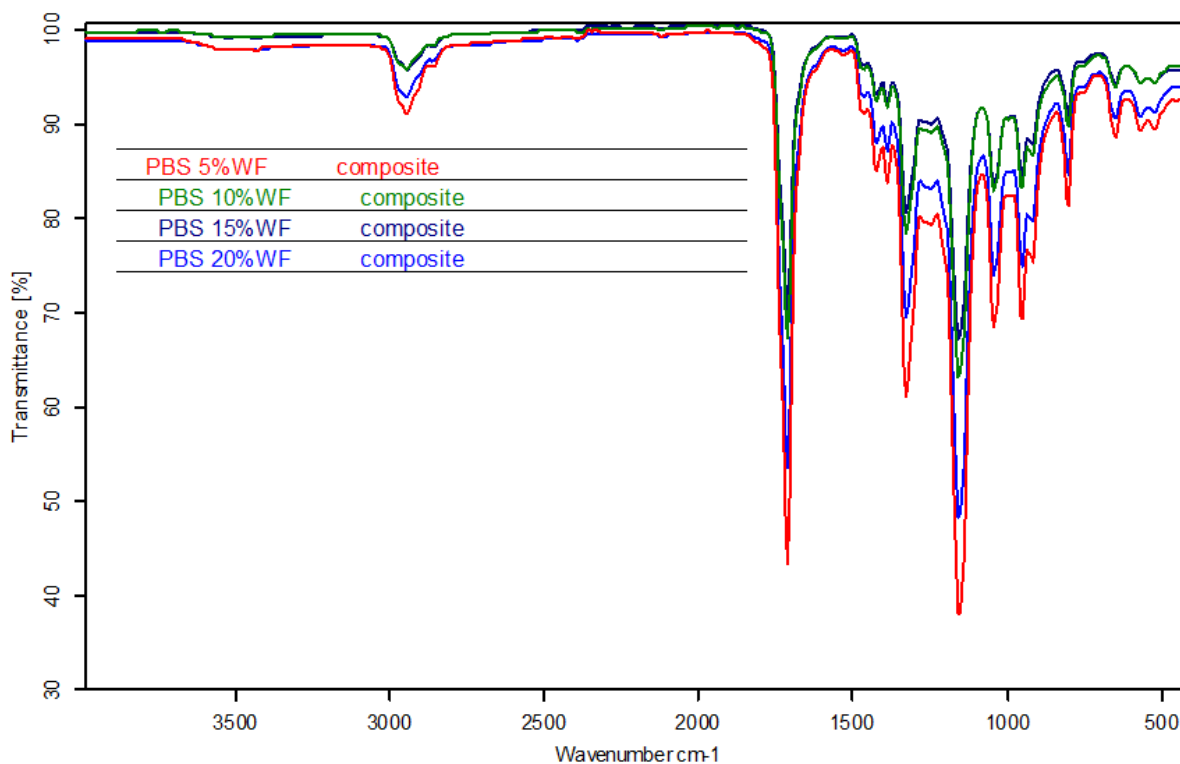


Figure 1. FTIR analysis of the PBS/PALF composites at the wavenumber range of 500 – 4000 cm⁻¹.

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3. ENERGY SAVING

Metal–Organic Framework Encapsulated with Polyoxometalates for Highly Stable Asymmetric Supercapacitors

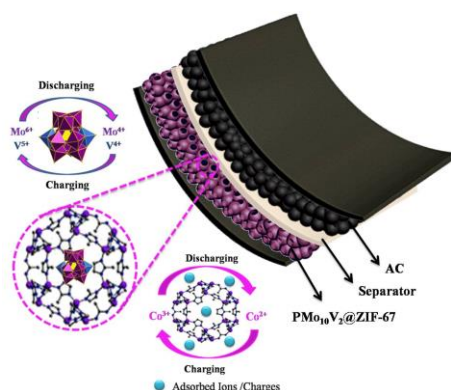
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Herein, we report on a facile one pot synthesis of polyoxometalates encapsulated zeolite imidazolate framework cages (POM@ZIF-67). The morphological and structural properties of the as synthesized materials were investigated *via* FESEM, EDS, XRD and FTIR techniques. Moreover, N₂ adsorption/desorption isotherms and XPS measurements were carried out to elucidate the textural properties and composition of the fabricated materials. Upon their use as supercapacitor electrodes, the POM@ZIF-67 electrode exhibited a maximum specific capacitance of 765 F g⁻¹ at a scan rate of 5 mV s⁻¹. Furthermore, a supercapacitor device was assembled using activated carbon as the negative electrode and POM@ZIF-67 as the positive electrode, delivering a specific power of 702 W kg⁻¹ and a corresponding specific energy of 20.9 Wh kg⁻¹ at a charging current density of 1 A g⁻¹. In addition, the device shows an excellent long term stability and high Columbic efficiency over 5000 charging and discharging cycles at a charging and discharging current density of 5 A g⁻¹.



A schematic diagram for the assembled POM@ZIF-67//AC asymmetric device.

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Photocatalytic activity of ZnO and Al-ZnO nanocatalysts for organic dye degradation under UV irradiation

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Through a simple chemical route ZnO and Al-ZnO were successfully synthesized. Fourier Transform Infrared Spectroscopy (ART-FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM), were used to investigate the functional groups, structural, morphological properties respectively. The resultant nanocatalysts were used forward to examine the influence of virous parameters (pH, concentration of dye, contact time, and catalyst dosage) on the photocatalytic degradation of organic dye (MO) under UV irradiation from aqueous solution. Al-ZnO demonstrate an exceptional (MO) degradation efficiency of 98-80 % at a large range of pH in comparison to ZnO photocatalytic degradation under the optimized conditions.

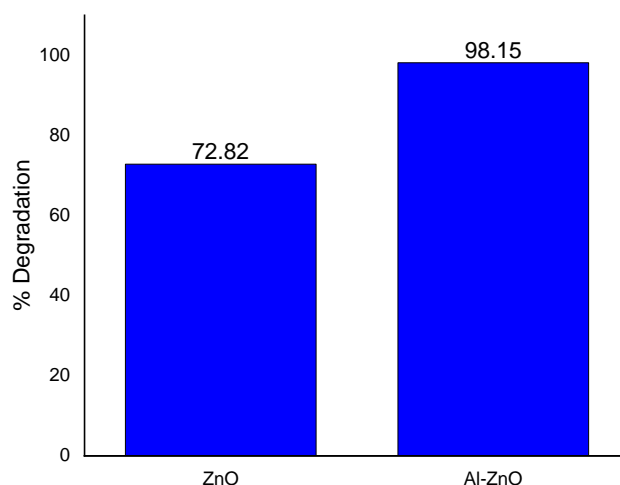


Figure 1. Photocatalytic degradation of (MO) under the optimized conditions using ZnO and Al-ZnO

Betacyanin geometrical isomers and their conformers with selected organic sensitiser (L0) in forming complexes dye towards dye sensitised solar cell application

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Abstract

Density functional theory (DFT) techniques examine dye geometrical structures, complexes and conformers employing isolated, cluster and slab systems. The geometric bent and planar structure initiate the investigation utilising Firefly 8.2.0/B3LYP/6-31G(d,p). Then, Gaussian, GW 16/B3LYP/6-31G(d,p) basis set and CAM functional realise the adsorption properties of the cluster and Vienna Ab initio Simulation Package (VASP) for slab system. The formed L0-1-Bd and L0-2-Bd complexes improve the betacyanins functionality more than isolated betanidin dye. The thermodynamic technique was used to analyse the isomerisation reaction between each of the two structural isomers investigated. The chromophore structure of zwitterionic and nonionic betanidins improves the isolated dyes' absorption and emission spectra in the visible and near infra-red areas with maxima wavelengths 428–511 nm and 565–965 nm, respectively. Zwitterionic favoured absorption and fluorescent properties more than adsorption to the TiO₂ anatase because intramolecular hydrogen bonding is away from the surface. Anchoring groups in the structure like -OH, which is not directly involved in TiO₂ adsorption during optimisation, must function as a lateral anchor. Lateral anchor in the direction of the adsorption surface, rather than away from it, may result in the better characteristics required for use in DSSCs. Simulated dyes@TiO₂ using crystal models: the TiO₂ slab and the hydrogenated (TiO₂)₆ cluster. For the slab, VASP via PBE functional and the cluster, GW 16/B3LYP/6-31G(d,p) in optimisation and CAM-B3LYP/6-31G(d,p) for spectro-electrochemical characteristics. Slab adsorption energy ranges between 1.934–1.970 eV and 6.66–7.57 eV for (TiO₂)₆ cluster at the same attachment site. The energy difference between the two binding models was found to correlate to the TiO₂ anatase sublimation enthalpy, depending on the role of intramolecular hydrogen bonding toward the adsorption surface. For natural dyes, one can anticipate systematic modification of the sensitiser building block to take into account the pigment chromophore structure. In the needy of the lateral anchoring group investigation, the effect on the adsorption to the TiO₂ surface is of significance. The mutual activity of the good anchoring group, the contribution of lateral anchor, appropriate binding mode and intramolecular H-bonding may result in the invention of novel materials with desirable properties for use in DSSCs applications.

Keywords: betanidin; zwitterionic/nonionic; betanidin complex; decarboxylated betanidin complex; DFT/TD-DFT

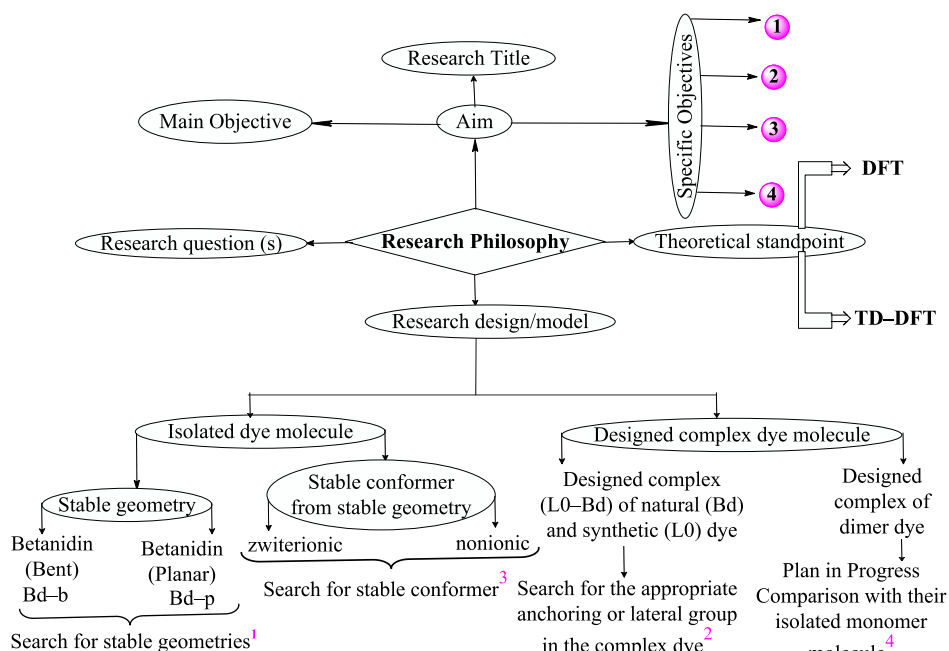


Figure 1: The research philosophy describes the fundamental tenets of the study

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Development of a flow platform for the synthesis of perovskite single crystals

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During the recent years, the interest in organic-inorganic perovskites for the development of photovoltaic materials has notably risen. These materials stand out due to their highly tunable properties depending on the chemical composition and the ease of synthesis in mild conditions employing solutions. Perovskite-based solar cells have reached efficiencies up to 24% [1], turning them into an alternative to silicon and a highly interesting topic in the development of renewable energies.

Classically, perovskite-based photovoltaic devices have employed layers composed of nanocrystals, however, the grain boundaries impose a limit to their maximum efficiency. Single crystals are proposed as a solution to this problem, but their synthesis raises new challenges due to lack of control during crystallization.

The development of an automated flow platforms aims to enhance the reproducibility of the process and, therefore, reduce the resources consumption. The proposed system is based in the Inverse Temperature Crystallization (ITC) technique [2]. This allows to obtain single crystals in a faster fashion than using classical crystallization techniques, a few hours instead of days, and without the need of additional materials like antisolvents. The central body of the system is manufactured employing 3D printing, the material used in the fabrication allows to have improved nucleation control.

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Keywords: flow, 3D-printing, perovskite

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Sonochemically synthesized cobalt oxide nanoparticles as an additive for natural polymer iodide electrolyte based dye-sensitized solar cells

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Hydroxypropyl cellulose (HPC)-based gel polymer electrolytes with different alkali metal iodide salts (potassium iodide, KI; sodium iodide, NaI; and lithium iodide, LiI) were investigated. Electrochemical impedance spectroscopy (EIS) was used to examine the electrochemical properties of the electrolytes. The electrolyte containing KI salt (KI sample) has the highest ionic conductivity. The trend of conductivity of the samples developed as follows, KI > NaI > LiI. A hybrid gel polymer electrolyte (HGPE) was developed to further enhance the property by incorporating sonochemically synthesized cobalt oxide (Co₃O₄) nanoparticles into the KI sample. The nanoparticles were studied by field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). HGPEs containing various amounts of synthesized Co₃O₄ nanoparticles were examined with EIS, XRD, and Linear Sweep Voltammetry (LSV). The introduction of Co₃O₄ nanoparticles has improved the ionic conductivity, reduced activation energy and degree of crystallinity of the HGPEs. Dye-sensitized solar cells (DSSCs) assembled with the developed HGPEs have shown an improvement in short-circuit current density and efficiency. HGPE containing 7 wt.% of Co₃O₄ nanoparticles achieved the best ionic conductivity and photovoltaic performance of DSSC of 8.02 mS cm⁻¹ and 5.8%, respectively.

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Optimization of the Oxygen Evolution Reaction through electron spin control in photoelectrochemical water splitting

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There is an urgent need to invest in more green and sustainable renewable energy sources taking into account the increase in the global population.^[1] Hydrogen, has no carbon, thus is a promising fuel source that can replace the popular non renewable hydrocarbon fuels; hence can be referred to as fuel of the future^[2] Green hydrogen produced by photoelectrochemical (PEC) water splitting has great potential as a fuel, considering the abundant sunlight and water sources.^[3] However, PEC can only be a groundbreaking innovation for the future energy security only if the challenges associated with PEC are addressed. This high overpotential associated with the process makes it uneconomic and inefficient. The Oxygen Evolution Reaction (OER) which occurs at the anode has been identified as the main source of the high overpotential.^[4,8] During PEC, when a chiral or ferromagnetic photoelectrode is used, the spin of the transmitted is controlled ensuring that the electrons left on the hydroxyl (OH) radicals have the same spin, opposite that of the transmitted electrons. The chiral molecules are potential generators of high spin-filters which is necessary to optimization of the PEC.^[5] This enhances selectivity and promotes the production of the triplet oxygen molecule and suppression of hydrogen peroxide.^[7-11] Experimental observations have revealed that hydrogen peroxide formation is a competing process to the OER during water splitting, and affects the stability of the photoelectrodes.^[8-9,11] However the concentration of hydrogen peroxide significantly reduced on the chiral electrode as observed in figure 1. Experimental observations and DFT calculations confirm that the control of spin through the CISS effect has a positive effect on the process. The control of electron spin, when aligned in their parallel state is paramount to the generation of the triplet oxygen molecule.^[9-11] This finding is essential in optimizing the oxygen evolution reaction. In this study the importance of spin alignment is highlighted as a necessity to the optimization of the OER in photoelectrochemical water splitting.^[9-11]

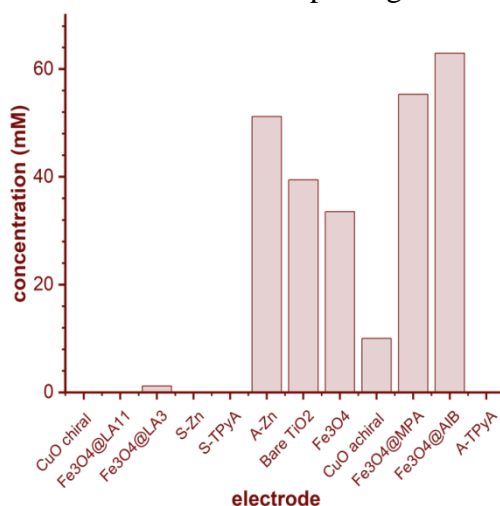


Figure 1. H₂O₂ Concentration calculated from the calibration curve obtained from reference^[6].

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Chiral metal organic frameworks in photoelectrocatalytic water splitting

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High overpotential and poor stability of the photoelectrodes ^[1] have been identified as some of the factors that affect the efficiency of the water splitting process. Metal organic frameworks have been synthesized according to the method reported by Liu ^[2] with terephthalic acid as a linker and Fe as the metal coordinating center. Chirality was introduced during synthesis by substituting a portion of the terephthalic acid with the chiral linker of either (R-) / (S+) camphor Sulphonic acid. FTIR measurements confirmed the successful formation of MIL-53, while the phase analysis was carried out using X-Ray Diffraction. Chiral photoelectrodes were fabricated by functionalizing TiO₂ nanoparticulate films with 0.1mM slurry solutions of MIL 53 R, MIL 53 S and MIL-53 L cysteine using the drop casting method. Water splitting was performed using functionalized TiO₂ nano particulate films. Linear Sweep voltammetry measurements were conducted in 0.1M Sodium Sulphate solution. Chronoamperometry measurements were performed at 0.50 V versus the Ag/AgCl reference electrode while chopping the light ON/OFF. All photoelectrochemical measurements were carried out in a 3 electrode system using the Ag/AgCl reference electrode and a platinum counter electrode. The chiral photoelectrodes produced high photocurrent densities and have demonstrated potential as efficient hydrogen production photoelectrocatalysts.

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SuperCapattery: Trump card of NexGen Vehicles

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Current generation is moving towards fully sustainable renewable energy source community replacing fossil fuels with hydroelectric, solar and wind energy accompanied with energy storage devices to create a greener world and to save up the limited fossil fuels. Energy storage device particularly batteries are essential power up the crucial applications. But Li-ion batteries are not environmentally friendly and take several hours for recharging whereas supercapacitor has energy density is much lower than batteries. So, a hybrid device known as **supercapattery** was developed by combining supercapacitor and battery type electrode to achieve overall splendid electrochemical performance suitable for electric vehicles. Recently, a 2D metal carbide/nitride family known as MXene has been explored due to its large surface area, tunable hydrophilicity contributing to its surface redox, abundant surface functionalities and its excellent electrical conductivity [1]. However, they suffer from restacking leading to drop in its electrochemical performance. Thus, herein binary nickel oxide nanoparticle (NiO NP) has been incorporated into Zirconium nitride (Zr_2N) MXene to increase the interlayer spacing of the Zr_2N MXene to prevent restacking of MXene and concurrently create synergistic effect between them to boost the physiochemical properties of the battery type electrode and exhibit splendid energy density without compromising its power density. The novelty of this work is the electrodes are developed as binder-free electrode with utilization of new exfoliation technique (atmospheric plasma method) which enhances light weight and wonderful conductivity.

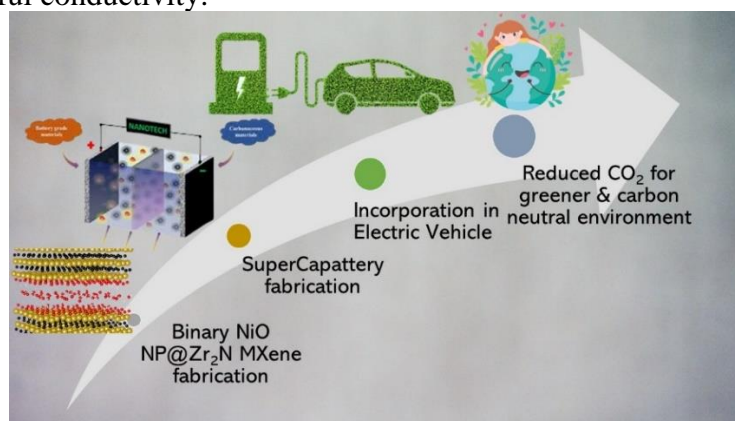


Figure 1. Illustration of the overview of the research plan.

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Ion beam induced modification of structural, optical and electrical properties of polypyrrole-methylammonium tin iodide (PPy-MASnI₃) nanocomposite films for photovoltaic applications

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The growing demand of energy as a result of the rapid growth of the global population and industrial evolution is a big challenge due to the depletion of fossil fuels and high energy consumption (Weiss et al., 2016). The burning of fossil fuels causes greenhouse gases which pose serious health problems to humans and affects the ecosystem therefore, development of eco-friendly clean energy sources is crucial (Kannan and Vakeesan, 2016). Perovskite solar cells are a rapidly growing technology in the field of photovoltaics with the aim of developing the alleged third-generation solar cells potentially to redefine their industrial utilization (Girish et al., 2022). Even though they exhibit high power conversion efficiencies their industrial utilization is still hindered due to their instability to changing environmental conditions (Mary Vijila et al., 2019). Conducting polymer additives are a subject of interest for improving environmental stability of perovskites stability by controlling the morphology (Sardar et al., 2022). In this research CH₃NH₃SnI₃ crystals will be synthesis by spin coating and polypyrrole will be synthesized from the monomer pyrrole. The conductivity of polypyrrole will be further modified through ion beam irradiation. Then, CH₃NH₃SnI₃/PPy composite will be synthesised than the effects of swift heavy ion irradiation on polypyrrole on the structural, optical and electrical properties nanocomposites for potential applications in environmentally stable and high efficiency solar cells will be investigated.

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Preparation, characterization, and electrochemical evaluation of nickel sulphide on lignin-derived carbon material for supercapacitors

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Porous carbon is the main important component in energy storage systems. The production procedures for carbon materials should be cost-effective and use renewable materials, which is considered a green approach to produce energy [1]. Supercapacitors (SCs) have been of interest due to their high-power density, rapid charge/discharge, and long life [2] but they are disadvantaged by their low energy density [1]. Promoting the specific capacitance of electrode materials is often considered in order to improve their specific capacitance of electrode materials. The improvement of carbon-based materials has little effect hence there is a focus on the development of transitional metal sulphides such as nickel sulphide (NiS) as electrode materials for electrochemical performances. In this study, lignin was successfully extracted from black liquor by H₂SO₄ and used to prepare activated carbon. NiS nanoparticles and NiS/L-AC were prepared by a power-controlled microwave. All materials were characterized by FTIR, TGA, BET, XRD, SEM, and TEM and electrochemically analysed by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy.

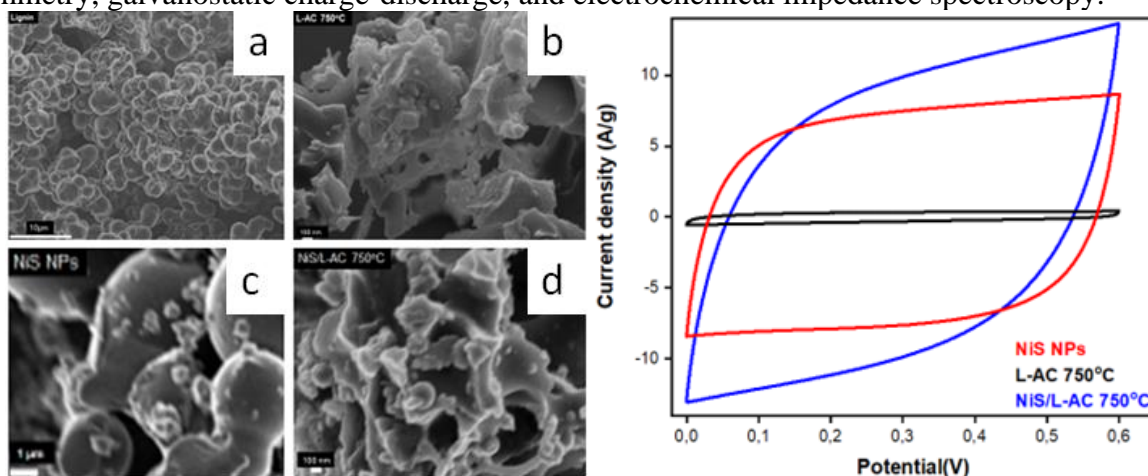


Figure 1: (a) SEM images of lignin, (b) L-AC 750°C, (c) NiS NPs and NiS/AC 750°C (d) CV curve of NiS NPs, L-AC 750°C and NiS/L-AC 750°C.

It was observed that lignin morphology forms pebble-like granules with a smooth surface (Fig. 1a). NiS NPs (Fig 1c) morphology has a spherical appearance but aggregates severely to form large micro-sized agglomerates. L-AC 750°C (activated carbon activated at 750°C, Fig. 1b) exhibits irregular shapes and agglomerated particles while NiS/L-AC 750°C (Fig. 1d) shows that NiS nanoparticles formed a composite with L-AC 750°C. Figure 1d shows a CV curve of NiS NPs, L-AC 750°C and NiS/L-AC 750°C at a scan rate of 100 mV s⁻¹ with a specific capacitance of 490, 254, 580 F g⁻¹ and energy density of 22.05, 11.43 and 26.1 Wh kg⁻¹ at a current density of 0.5 A/g respectively. These CV curves remain in good rectangular shapes even at higher scan rates, which displays a good current response and a good charge separation.

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Investigations of Earth Abundant Materials based Metal Oxide Photo-Electrodes for Solar Energy Conversion

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Nowadays, one of challenge mankind is facing to attenuate the critical issue of global warming, rapidly growing industrialization utilizes humongous amount of energy, energy demand is mainly supplied by the conventional energy sources, such as coal, natural gases, and oil. The excessive utilization of fossil fuels accompanied with large amounts of CO₂ emissions has led to the global energy and environmental crisis. Modern society needs a clean, sustainable, and low-cost method to store solar energy as solar is a vastly abundant resource that can match our present-day energy consumption. Hydrogen is a strong candidate for stored solar energy with high gravimetric energy density, no harmful byproducts upon combustion and the ability to be renewably produced from water using the photoelectrochemical (PEC) approach. For practical PEC, semiconductors are required that can fulfill a stringent set of physical and chemical requirements to perform water splitting efficiently and inexpensively.^{1,6}

This research work will focus on issues by developing different technologies. Hydrogen is considered as fuel in powering nonpolluting vehicles, domestic heating, and aircrafts. Water and Sunlight offers alternative source to produce hydrogen apart from fossil fuels and biomass. Photo electrochemical (PEC) water spiting is useful technique for clean solar Hydrogen production. In 1972, Honda and Fujishima first investigated water splitting using a single TiO₂ crystal as photo anode and Pt as a cathode.⁷ The CuO@CuFe₂O₄ core–shell structure is one of the new Concept for the facile fabrication of photocathodes in PEC application.⁸

Secondly, current research work will focus on issues by developing technologies to capture and convert carbon dioxide (CO₂) a greenhouse gas and by finding alternative source of clean and renewable energy to minimize consumption of fossil fuels and photocatalytic (PC) and photo-electrochemical (PEC) reduction of CO₂ into fuel utilizing solar energy could address both problems and have receive increasing attention. PEC reduction of CO₂ is promising and research on this subject increased rapidly,⁹ Some scientists worked on specific target products.¹⁰ Focus of most recent work is on development of photoelectrodes to increase its selectivity, activity, and stability to make more economical.

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Complex processing of high-silicate phosphate ore in the scheme with recycling

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Abstract: In order to obtain monohydrate of monocalcium phosphate for agricultural purposes and the associated product - silicon dioxide (alpha quartz) for use in the glass industry, the possibility of complex processing of non-standard siliceous phosphate ores using a mother liquor recycle is shown. The characteristics of the processed products and their compliance with the regulatory requirements for the quality of fertilizers and glass are determined. To improve the environmental safety of monocalcium phosphate monohydrate used in greenhouses in closed areas, it is necessary to clean it from sorption-trapped chlorine impurities accumulated in the soil by washing and recrystallization. To improve the quality of technical alpha quartz extracted from phosphate ore, it is advisable to remove Fe^{3+} + impurities by magnetic separation.

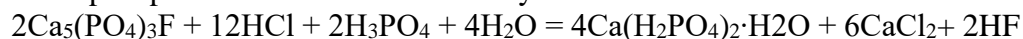
1. Introduction

Every year, approximately 150 million tons of phosphate raw materials are extracted in the world to produce mineral fertilizers designed to increase soil fertility. The need for them increases with the growth of the population. This leads to a reduction in the reserves of high-quality raw materials and requires the involvement in the processing of low-grade types of phosphate ores with a high content of impurities, including toxic elements. At the same time, the risk of soil contamination with toxic elements increases [1]. This problem is particularly relevant in conditions when closed greenhouse lands are used in crop and vegetable production, where toxic substances accumulate.

High-quality phosphate ores with a P_2O_5 content of 39-42% by weight are used in the production of phosphoric acid, and non-standard ones with a low P_2O_5 content of 19-21% by weight are used as fertilizers after grinding [2,3]. Some phosphate ores are a promising source of rare earth elements. However, the costs and technical problems caused by the low content of the latter hinder the development of technologies for their extraction [3,5].

Production of phosphorous fertilizers is carried out by methods of acid decomposition of natural phosphate ores. The development of integrated processing methods applicable to both high-quality and low-quality phosphates [6] is important for solving environmental problems and improving the economic efficiency of technological processes [7].

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is an agricultural product that is used for all types of agricultural structures. The physico-chemical basis for the production of monocalcium phosphate monohydrate consists in the acid processing of natural phosphate ores and is described by the main reaction:



The most economically feasible is the recirculation production technology, which allows the use of non-standard phosphate raw materials with a low phosphorus content (15-23% P_2O_5) and a high content of ballast impurities (SiO_2 , Al^{3+} , Fe^{3+} , etc.). To obtain a conditioned product with a given ratio of Ca:P=1:2 an additional source of phosphorus, H_3PO_4 , was used. High decomposing activity was provided by HCl. Reagent selection and process parameters: concentration, ratio of L:S, temperature, and hydrodynamic regime, which ensure the decomposition coefficient of phosphate ore of at least 98%, were determined experimentally [8].

As a result of hydrochloric acid extraction of siliceous phosphate ore [1,2,4, 9], monocalcium phosphate monohydrate of various quality was obtained: 1-technical product $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ + $\text{SiO}_2 + \text{Fe}^{3+} + \text{Al}^{3+}$, 2- $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ purified by crystallization, 3-purified by double crystallization. As

a result of the decomposition, an insoluble residue was formed in the form of alpha quartz, which was subjected to washing with distilled water.

Specifications for compliance with the requirements of monocalcium phosphate monohydrate normalized indicators of the quality of the product is the concentration of P_2O_5 (55-56%) and toxic substances: arsenic (0.005%), fluorine (up 0.2%) and lead (no more than 0,002%).

The main advantages of recycling technology are: energy Efficiency, sustainability, environmental management resources, and as a consequence, the efficiency of the process.

2. Materials and methods

The objects of the study were: samples of siliceous phosphate ores with a particle size of 0.315-1.0 mm, phosphoric acid of the qualification "ch. d. a" (GOST 6552-58), hydrochloric acid of the qualification "O. S. ch." (GOST 14261-77), distilled water (GOST 6709-72).

To determine the content of the components, we used: titrimetric, complexometric, photocolorimetric and ionometric methods of analysis.

The physical and chemical analysis of the test sample was performed using a photoelectric colorimeter KFK-3-01 (ZOMZ, RF), a polarizing microscope MIN-8 (LOMO, RF), a specific surface area analyzer Sorbi-MS (Meta, RF), complete with a sample preparation station SorbiPrep (Meta, RF), a compact auto-titrator G20 Mettler Toledo (Mettler-Toledo GmbH, Switzerland), and a pH meter-ionomer expert-001 (Econix–Expert, Russia).

3. Results

The fractional and chemical composition of a non-standard high-silicon sample of phosphate ore was determined (Table 1). It is shown that the impurities are evenly distributed over the fractions of the test sample [10, 11, 12] and its primary enrichment by fractionation is inefficient [9] due to the close relationship of phosphate and siliceous minerals [13,14].

On the example of the hydrochloric acid method, the possibility of obtaining the main product is shown $Ca(H_2PO_4)_2 \cdot H_2O$ of different quality (Figure 1) and a related product-an insoluble residue in the form of SiO_2 from ore of the composition: $Ca_{10}(PO_4)_6CO_3$

High decomposing activity was provided by HCl. To obtain a conditioned product with a ratio of Ca:P=1:2 an additional source of phosphorus, H_3PO_4 , was used. Reagent selection and process parameters: concentration, ratio of L:S, temperature, and hydrodynamic conditions that provide a decomposition coefficient of at least 98% of phosphate ore were determined experimentally [7].

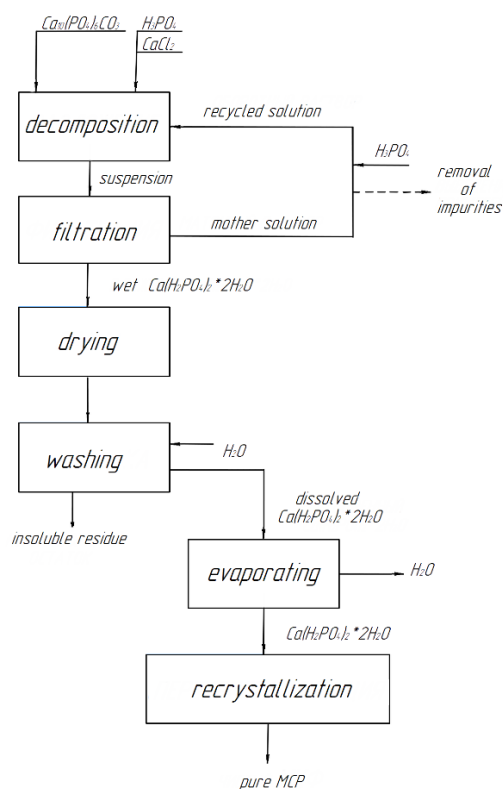


Figure 1. Block diagram of the production of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ by recirculation technology
 Table 1. Chemical and fractional analysis of non-standard high-silicon phosphate ore

Fraction, mm	fraction output, %	Fraction composition, %							
		P_2O_5	output P_2O_5	CaO	MgO	Fe_2O_3	F	Cl	*I.R. including SiO_2
6.0 – 5.0	2.23	13.58	1.98	25.31	1.27	6.97	0.005	0.001	35.79
5.0 – 3.0	5.07	14.52	4.81	21.93	0.78	6.58	0.005	0.001	35.96
3.0 – 2.0	7.92	15.26	7.90	22.87	0.31	3.62	0.006	0.001	34.33
2.0 – 1.0	11.39	17.14	12.76	26.80	0.20	3.29	0.009	0.001	33.38
1.0 – 0.5	17.02	15.50	17.24	28.24	0.10	3.02	0.008	0.001	34.85
0.50 – 0.355	10.81	17.31	12.23	30.00	0.10	2.96	0.008	0.001	33.11
0.355 – 0.315	4.19	15.44	4.23	28.29	0.21	2.96	0.009	0.001	35.42
0.315 – 0.18	13.83	15.64	14.14	28.39	0.30	2.56	0.007	0.001	37.78
0.18 – 0.09	17.62	12.61	14.52	28.90	0.10	3.16	0.008	0.001	47.18
0.09 – 0.071	3.07	12.48	2.50	27.40	0.21	2.83	0.009	0.001	48.31
< 0.071	6.84	15.77	7.05	26.05	0.20	2.63	0.012	0.001	39.26

* I.R. – insoluble residue

4. Discussion

Recirculation production technology is the most economically feasible, since it allows the use of non-standard phosphate raw materials with a low phosphorus content (15-23% P_2O_5) and a high content of ballast impurities (SiO_2 , Al^{3+} , Fe^{3+} , etc.).

As a result of the dissolution and filtration of product 1, an insoluble residue in the form of alpha quartz was isolated, the characteristics of which are presented in Table 2 after washing with distilled water [15].

Table 2. Technical Requirements of Raw Materials for the Production of Glass of different Grades and Kinds

Raw material	Application	Weight content, %, components		
		SiO ₂ , not less than	Fe ₂ O ₃ , not more than	Al ₂ O ₃ , not more than
Quartz sand and vein quartz, beneficiated, highest grade	Production of optical glass operating at small thickness, lead crystal, artistic articles, uviol glass	99,80	0,01	0,10
Quartz sand and vein quartz, beneficiated or unbeneficiated, highest grade	Manufacture of illumination and signal glass, high-quality glassware, pressed articles obtained by 'duralex' mechanized manufacturing process, sodium silicate (catalysts)	99,00	0,02	0,40
Quartz sand, ground quartzite and quartz vein quartz, beneficiated or unbeneficiated, grade 1	Manufacture of sheet, window, and technical glass, laboratory, medical, and perfume glass, glass fiber for electrotechnology, sodium silicate (catalysts)	98,50	0,04	0,60
Quartz sand, ground quartzite and ground vein quartz, beneficiated or unbeneficiated, grade 2	Manufacture of insulators, tubes, glass cans and bottles from semiwhite glass, glass fiber for construction and other applications	95,00	0,10	2,00
Quartz sand, ground sandstone, ground quartzite, and ground vein quartz, beneficiated or unbeneficiated, grade 2	Manufacture of glass fiber for construction purposes, glass cans and bottles from the semiwhite glass, insulators, tubes, foam glass, battery cells	95,00	0,15	2,00
Quartz sand, ground sandstone, ground quartzite, and ground vein quartz, unbeneficiated, blended	Manufacture of foam glass, glass fiber for construction purposes, glass cans and bottles from semiwhite glass, insulators, tubes, battery cells	95,00	0,25	4,00
Quartz sand, ground sandstone, ground quartzite, and ground vein quartz, unbeneficiated	Manufacture of green bottle glass	95,00	Unnormalized	4,00

Subsequent washing and recrystallization of product 2 allows to obtain a purified product 3 $\text{Ca}(\text{H}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ for use in greenhouses and as animal feed.

The resulting monohydrate of monocalcium phosphate from the first stage of production is suitable for crops cultivated on large areas. After the second stage (recrystallization) of $\text{Ca}(\text{H}_2\text{O}_4)_2$ suitable for protected soils and animal husbandry.

5. Conclusions

The disadvantages of this technology are: the frequency of the process, the production of a contaminated finished product, but it can be processed by the recrystallization process, to ensure the appropriate quality required for the product. Formation of an insoluble residue in the form of SiO_2 , which can be used in the glass industry [8].

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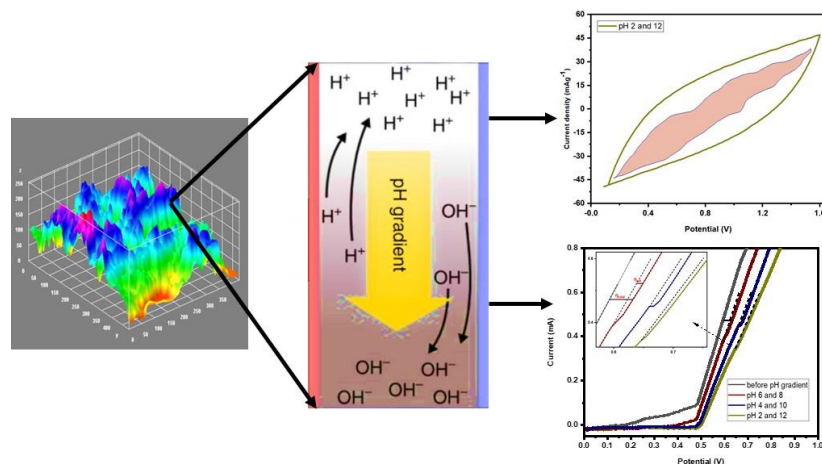
pH based supercapacitors: Achieving high capacitance in gold metallized regenerated cellulose amide supercapacitor electrodes by pH gradient

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High energy density was achieved through pH gradient creation in an amidic cellulose incorporated with gold nanoparticles. Three different pH gradients (6-8, 4-10, and 2-12) showed respective specific capacitances of 218, 423 and 603 Fg^{-1} energy densities of 34, 67 and 96 WhKg^{-1} . The pH gradient overpotentials were 0.011, 0.014 and 0.020 V for the three respective pH gradients, where the electrode having the highest overpotential had the highest energy density. The electrode with a pH gradient of 2-12 had the lowest diffusion-based activation energy of 1.358 KJmol^{-1} , and the highest diffusion current. This work successfully shows that pH gradient contributes to an additional diffusive current in supercapacitor electrodes and the diffusion current improves the overall specific capacitance. The work also shows that pH gradient creates an overpotential that consequently improves the energy density of the electrodes. The retention capacities of 94%, 92% and 91% were obtained for the 6-8, 4-10 and 2-12 respective pH gradients, to establish that pH gradient had no obvious effect on the retention capacity of the electrodes.



Stabilization of compressed earth blocks (CEB) by pozzolana based phosphate geopolymer binder: physico-mechanical and microstructural investigations

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The housing crisis affects more than half of the African population. In Cameroon, earth has historically been used as a building material for many years. The development of ordinary Portland cement (OPC) has reduced the use of earth materials in the building and construction industry [1, 2]. The development of low cost and sustainable is feasible in country like Cameroon due to the abundance of natural resources such as aggregates, earth (clay, laterite and natural pozzolan) in all regions [3]. This work proposes the poly(phospho-ferro-siloxo) binder resulting from the phosphoric acid activation of pozzolana (PZ) as a friendly stabilizing agent for compressed earth bricks (CEBs). Different proportions of pozzolana were incorporated into the clay soil (5, 10, 15 and 20 wt%). The CEBs were cured at 25°C and at 70 °C. Powder X-ray diffraction (PXRD), Fourier transformed infrared spectroscopy (FTIR), water absorption as well as mechanical strength tests were used to characterize the 28 days aged CEBs. The compressive strength of CEBs varies from 9.2 to 20.6 MPa and 10.2 to 42.8 MPa at 25°C and 70 °C, respectively. Water absorption ranges from 6 to 11% at 25 °C and 8 to 12% at 70 °C. These results indicated the possibility to use pozzolana based phosphate geopolymer binder as efficient stabilizer for the development of structural and functional CEBs. Pozzolana based phosphate geopolymer binder appears as energy-efficient and sustainable solution for the stabilization of CEB.

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3D Printable Liquid Crystal Elastomers with Light-Induced Shape Transformations

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Liquid crystal elastomer (LCE) having reversible anisotropic properties, shape-morphing response, and programmable microstructure is a potential ink for 3D printing to manufacture stimuli-responsive shapes and smart materials.¹⁻³ Along with its elastomeric and rheologic character, LCEs are excellent choice for fabrication of these dynamic architectures.¹ LCEs are known to have thermal actuation responses.^{1,2} However, energy concerns and rapid local control of thermal actuation limit the shape-morphing applications³, thus current approaches are toward photoresponse. One method toward greener light actuation is to incorporate azobenzene groups in LCE mesogen.³ In this preliminary research work, we report a one-pot synthesis of a main-chain LCE oligomer and a photoresponsive azodye core molecule. Main-chain LCE oligomers were synthesized via aza-Michael addition of 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene and n-butylamine. Synthesis of the light-responsive mesogen (E)-diazene-1,2-diylbis(4,1-phenylene)bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) or D6OA was also successfully done. This light-responsive mesogen will later be incorporated with the native mesogen to produce the final LCE ink. ¹H-NMR analyses confirm the successful synthesis of both compounds. The development of a photoresponsive LCE ink for 3D printing is the initial step towards creation of smart objects with light-induced shape transformations, such as artificial muscle, biomedical devices, and soft robotics.^{1,2}

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4. HEALTH

CHARACTERIZATION OF *Archachatina marginata* and *Achatina fulica* SLIME AND
DETERMINATION OF THEIR ANTIMICROBIAL ACTIVITIES

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Archachatina marginata and *Achatina fulica* slime has been reported to exhibits various biological activities, such as antimicrobial, antioxidant, anti-tyrosinase, and antitumoral activities and great value in wound healing and repair, these active ingredients moisturize, firm the skin and fight against imperfections and skin aging.

Due to this effect, the aim is to determine the bioactive compounds in *Archachatina marginata* and *Achatina fulica* slime. The *Archachatina marginata* and *Achatina fulica* slime were extracted using mechanical method. Phytochemicals screening was done using standard method. Chemical profiling was determined using Gas Chromatography- Mass spectrophotometer (GC-MS). Antimicrobial screening of *Archachatina marginata* and *Achatina fulica* slime were carried out using Agar well diffusion method.

Archachatina marginata slime extract has higher percentage yields compare to slime extract of *Achatina fulica*. The phytochemical screening of *Archachatina marginata*-and *Achatina fulica* slime extracts show the presence of tannins and flavonoids. The GC-MS Analysis identified 108 chemical compounds in *Archachatina marginata* slime; the percentage area of the major chemical compounds identified in *A. marginata* slime extract was 73.79% while minor chemical compounds were 26.19%. The GC-MS analysis identified 122 chemical compounds in *A. fulica* slime extract; percentage area of the major chemical compounds identified in *A. fulica* slime extract is 69.32% while minor chemical compounds account for 30.68%.The antimicrobial screening of *A. marginata* slime and *A. fulica* slime extracts show that *A. marginata* slime has higher antimicrobial activities compared to *A. fulica* slime. The presence of various chemical compounds in *A. fulica* and *A. marginata* slime revealed that the slime extracts possess many medicinal uses.

Fatty acids-based Eutectic Solvents Liquid Membranes for Removal of Sodium Diclofenac from Water

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Pharmaceuticals have a main role on health and life quality of humans and animals. Nevertheless 30% to 90% of all oral administrated drugs are excreted as active compounds [1], leading the worldwide occurrence of these active compounds and their metabolites in water sources, soils, and biota. As these compounds are designed to have a biological response to small dosages, they are an important threat to public health and ecosystem stability even at low concentration [1]. Additionally, their relative high stability is even more concerning, as the continuous ingestion of small doses can lead to accumulation since the degradation rate is slower than the up taking. On the other hand, conventional wastewater treatment plants (WWTP) are not designed to remove these compounds that enter the environment. Despite the report of diverse cases of life-threatening biological effects of these drugs on wildlife, about 88% of all pharmaceuticals do not have environmental toxicity data [2].

Although the use of eutectic solvents (ES) provides a cheap and efficient solution for the removal of APIs micropollutants [3 - 4], the toxicity of some of the used compounds and their leaching are drawbacks that need to be overcome to develop a fully sustainable system. The use of all natural compounds like sugars, amino acids, organic acids, choline and urea that exhibit low toxicity and have a high biocompatibility might be the answer for this problem.

In this work, ES based on fatty acids were impregnated on porous membranes by soaking and used to remove sodium diclofenac from water using UV-Vis spectroscopy to quantify the extraction efficiency of the membranes. Experimental parameters such as contact time, number of membranes, pH and initial concentration of pharmaceutical were optimized to achieve a remarkable extraction efficiency 97%. These membranes were re-used over 9 more cycles of extraction without decreasing the efficiency.

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Caffeine tablet formulation targeted at a delayed drug release profile

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Solubility is one of the most important drug properties that needs to be assessed and addressed for efficient drug metabolism and therapeutic activity.

In this study, we assessed a formulation of caffeine tablet targeted at achieving 50% solubility within 4 hours (240 minutes). The physicochemical properties of Caffeine were carefully studied and considered when choosing various excipients used; lubricants, glidants, fillers and matrix. All excipients including the Active Pharmaceutical Ingredient (Caffeine) were quantitatively measured at appropriate proportions and blended accordingly in a diffusion-based principled blender to have a homogenous mixture. Compressibility of the mixture was assessed before feeding into a single tablet punch pressing machine to make sure tablets produced have an improved compactness. The pressing machine was set to produce 500mg/tablet for uniformity in the experiment and all tablet were produced under the same condition to avoid error as much as possible. To measure and monitor the percentage drug release profile (disintegration); Two caffeine tablets weighing 470mg each were tested in a USP drug release tester containing distilled water at constant temperature and constant speed of the stirrer. Concentration of the water was recorded before putting the tablet and concentration of the water was recorded after placing the tablet in the USP drug tester at time interval using an Ultraviolet-visible spectroscopic method. The exact procedure was repeated for both tablet samples.

The measured concentration with respect to time shows that the formulation brought about a slow drug release: the result showed that there was 27.26% caffeine release at 240 minutes for tablet 1 and 25.60% caffeine release for tablet 2. In as much as we are far behind the targeted percentage, this formulation could proof useful for drugs intended for a more delayed release and prolonged activity in vitro such as tuberculosis drugs (rifampicin).

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Nanoemulsified Phytocapped Nanoparticles as Novel Antibiotics

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Recent interest in plant-based antibiotics is justified, as pathogens have developed resistance for conventional antibiotics. Metal nanoparticles (MNPs) synthesized using plant extracts have been shown to possess antimicrobial activities against multidrug resistant (MDR) bacterial. However, diversity and complexity present in the phyto-composition of plant extracts which in turn affects size, shape, crystal structure, purity, reproducibility, surface chemistry, and toxicity of MNPs has led to the urgent search for new and natural bioactive capping and stabilizing agents for the green synthesis of metal nanoparticles (MNPs). Also, the biosafety of MNPs is of major concern, especially in the medical industry. Recently, the use of pure pharmacologically active phyto-compounds as capping and stabilizing agents has been deployed to avoid toxic effects during the MNPs preparation and to enhance their drugability compared with conventional drugs. This research will focus on synthesizing MNPs using piperine and allicin isolated from fresh *Piper nigrum* (Black pepper seeds) and *Allium sativum* (Garlic cloves) respectively as capping and stabilizing agents. This MNPs will be incorporated into O/W nanoemulsion formulation prepared from *Azadirachta indica* seeds (Neem oil) and water. In-vitro and in-vivo antimicrobial tests will be carried out on the WHO's priority list of MDR bacteria isolates and Wistar albino rats respectively. This research will circumvent many drawbacks associated with MNPs synthesized using plant extracts as capping and stabilizing agents by giving a clearer understanding of the interactions between metals and active phyto-compounds, reducing MNPs toxicity and increasing their drugability. Also, this research will increase human chances against health problems, economic threats, and social risks posed by MDR pathogens most especially those on the WHO's list of priority pathogens for R&D of new antibiotics.

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Carbon nanotube-supported iron oxides enhance pollutant removal in wastewater

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Carbon nanotubes (CNT) are a carbon allotrope made of a hexagonal arrangement of sp²-hybridized carbons in a tubular structure. Over the years, they gained increasing attention for catalysis applications due to their chemical stability, thermal stability and electrical conductivity, besides their high specific surface areas. These properties increase the catalyst efficiency and durability. Hence, this work aims to investigate CNT-supported iron oxides prepared by wet impregnation for Fenton-stimulated degradation of rhodamine B (RhB), a carcinogenic persistent dye. This pollutant is often present in industrial wastewaters, giving an undesirable color and demanding its removal before being disposed of in natural waters. In pursuance of this goal, commercial carbon nanotubes were impregnated with iron at different concentrations (1, 5 and 10% w/w) and their activity in the Fenton reaction was evaluated. Characterization of the catalyst was performed by atomic absorption spectrometry, gas adsorption, x-ray diffraction and Mössbauer spectroscopy. UV-vis spectroscopy ($\lambda=554$ nm) was used to follow RhB removal using Fenton reaction over the catalysts. Gas adsorption-desorption isotherms show behavior of type I isotherms at low pressures and type IV isotherms at high pressures. Interparticle adsorption was also observed. BET method showed a relevant decrease in specific surface area and pore volume after impregnation with iron. Diffractograms obtained for the catalysts show the presence of iron oxides in the form of magnetite and hematite. Mössbauer spectroscopy confirmed the iron phases and elucidated the proportion between the phases. It was also possible to observe that at lower concentrations of Fe (1 and 5%), sub 10 nm particles were the majority. The 10% Fe-catalyst also showed a considerable number of bigger particles. The removal of RhB was observable by decolorization of the solution and was successfully followed by UV-vis spectrometry. CNT, the pure carbon nanotube, was capable of removing about 60% of the pollutant. This removal was associated with adsorption of the RhB on the nanotube walls. CNT1, impregnated with 1% of Fe, was capable of removing about 80% of rhodamine B. As expected, it was possible to increase removal by adding Fe to the reaction medium in order to promote the Fenton reaction. CNT5 and CNT10, 5% and 10% iron respectively, exhibited similar performance on the degradation. Therefore, CNT5 was deemed as more adequate for this application as it similarly removes RhB but saves about half the amount of iron. The effect of pH was evaluated and acidic media was considered more suitable for the removal of RhB. This effect can be attributed to the need of protons in the Fenton reaction. Acidic media promotes the Fenton and thus the removal of the pollutant by decomposition by hydroxyl radicals.

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Green Therapy For Malaria

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Malaria is said to have a tremendous impact on humanity and is one of the most serious and common infectious illness. Despite the fact that numerous measures have been used to eradicate malaria, it remains a major public health concern, particularly in areas where it has become endemic such as Africa. It is caused by mosquitoes, and it is transmitted to human by *Plasmodium falciparum*. Different measures like insecticides have been made for the eradication of the disease. But the use of a certain antimalarial drug on a regular basis causes the target malaria vector to acquire resistance. This study's overall aim is to develop a mosquito repellent paint through which *HYPITIS SUAVEOLENS* (Bush mint) will be extracted, by hand squeezing and by using solvent (distilled water and ethanol); and analyses of the pure extract were run using FT-IR. Mosquito larvae were reared, paints were formulated, and the paint was compounded with the pure extracts, and quality control analyses (like pH, density and drying time) were carried out on the compounded paints. Inhibition properties of larvae. The quality control parameters (pH, density, and drying time) of some of the compound extracts (those containing 2ml and 10ml extract) were accurate when compared with the commercial paint and they also follow the standard quality control parameters of Standard Organization of Nigeria (SON). The inhibition properties of the pure and compounded extract were checked on mosquitoes larvae, and it was revealed that the inhibition properties of that of ethanolic extracts is higher than the other extracts, followed by squeezed extracts which also perform really great in the inhibition; while that of cold and hot distilled water extracts have poor performance.

This work focused on the use of plant extract compounded with paint in control of mosquito in order to reduce the spread of malaria in the society, and to serve as an alternative to synthetic repellents which are harmful to human health and very expensive.

Human health risks associated with organochlorine pesticides level in soils in Eket agricultural zone, Akwa Ibom State, Nigeria

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The routine use of restricted organochlorine pesticides (OCPs), principally for pests control and boosting crop yield, has pose serious threat on soil, other environmental matrices and to health. In this study, the levels of thirteen OCPs were quantified in soils collected from six Local Government Areas (LGAs) of Eket agricultural zone, using gas chromatography-mass spectrophotometer (GC-MS). The levels were subjected to human health risk assessment models to predict possible risks to health resulting from ingestion, inhalation and dermal contact with the soil or farm produce. Results revealed that the levels of Σ OCPs in soil samples ranged from below detectable limits (BDL) to 8.179 $\mu\text{g/kg}$. High levels (0.949 – 8.179) $\mu\text{g/kg}$ were found for α -HCH across the zone and α -HCH was above the maximum permissible limit (MPL) of 7.4 $\mu\text{g/kg}$ in Mkpatak Enin. However, α -chlordane showed the lowest concentration across the zone with range BDL – 0.005 $\mu\text{g/kg}$. Non-carcinogenic risk was generally low as the computed hazard quotients (HQs) and hazard indexes (HIs) were less than unity. The incremental lifetime cancer risk (ILCR) value for Σ HCH (2.55E-03) is indicative of a moderate to high carcinogenic risk for children in Eket. ILCR values ranging from 1.98E-04 to 9.74E-12 for children and adult across all LGAs in the study area is indicative of a low to very low cancer risk in both age groups upon exposure via dermal absorption and oral ingestion pathways. OCPs were detected at varying levels and there is moderate to high exposure risk especially for children in the zone.

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Time-dependent mechanistic insight into photo-degradation of mixed hydrophobic disperse dyes by magnetically separable nitrogen iron codoped titania under visible light using process variable optimization

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This work reports the time-dependent mechanistic insight into photo-degradation of a mixture of Navy Blue 3G, Scarlet RR, Scarlet 3R dyes using visible light active and magnetically separable ternary γ -Fe₂O₃/N, Fe–TiO₂ prepared by the ultrasonic-hydrothermal method. In the present work, samples collected on an hourly basis over a period of 4 h to propose the time-dependent mechanistic pathway and formation of transient intermediates delineated by LC-MS analysis. The decrease in a number of transient intermediates formed with respect to time of degradation supported the effective mineralisation process of disperse dyes, known to be difficult to degrade due to their hydrophobic nature. After 4 h, only one major intermediate was obtained from Navy Blue 3G along with two minor intermediates from Scarlet RR were observed while Scarlet 3R underwent complete mineralisation. The optimization of process parameters was done by response surface methodology (RSM) based on central composite design (CCD). The degradation was monitored by UV and chemical oxygen demand (COD) analysis which indicated complete decolouration and degradation up to 78% under the optimum conditions of initial concentration 40 mg/L, pH 7.5 and with a catalyst loading of 1.0 g/L using 1.5 ml of H₂O₂ within 4 h as obtained by RSM. The enhanced activity of γ -Fe₂O₃/N, Fe–TiO₂ can be ascribed to a considerable shift in bandgap, enhanced surface area and generation of reactive species.

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

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Water management However, heavy metal ion contamination and wastewater treatment are difficult tasks all over the world due to the impact on human health. This study focuses 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, the FTIR, XRD, TGA, and BET analysis results have shown that the synthesis of BCS/DAPTMS composites via in-situ sol-gel process was successful. FT-IR spectroscopy, N₂ adsorption-desorption, and DTA/TGA measurements were used to investigate the chemical and textural properties of the mesoporous synthesized. FTIR analysis confirmed the removal of hemicellulose and lignin, and silica and amino groups were successfully grafted onto the bleached cellulose (BC) backbone. The BET analysis revealed that mesoporous BCS/DAPTMS improved their thermal stability significantly. The surface area of BCS (1,2662 m²/g) is greater than that of BC (0,172 m²/g), indicating that the hydrophobicity of BCS has improved. Because pore size and surface area are inversely proportional to pore volume, larger pore size and surface area result in lower pore volume. The X-Ray diffractograms show a major diffraction peak around $2\theta = 22^\circ$, which is attributed to the intensity of BC, BCS, BCS-DAPTMS (2,4 & 10%); and a broad diffraction peak was also observed between $2\theta = 15^\circ$, corresponding to the amorphous region and crystalline area of Cellulose. Only one major diffraction peak for silica was revealed around $2\theta = 22^\circ$. The findings indicated that the crystalline state of BC was not destroyed by the Silica & silane coupling agent, and that the crystallinity index values increased.

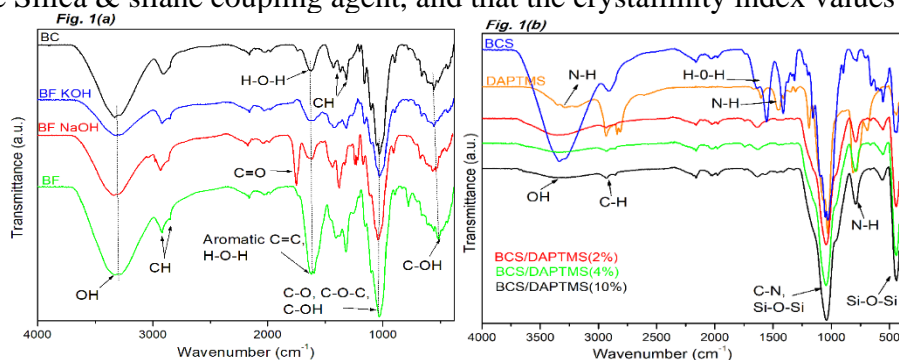


Figure 1. (a) FTIR spectra of Bleach Cellulose extraction step-by-step, (b) FTIR spectra of BCS, DAPTMS, BCS-DAPTMS (2,4 & 10%)

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Molecular Imprinted Polymers (MIPs) for selective extraction of Per- and Poly-fluoroalkyl substances (PFA) from water systems.

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Per- or poly-fluoroalkyl substances (PFAs) are organic compounds whose hydrogen atoms are either partially or entirely replaced by fluorine atoms [1]. Due to their water, oil, and dust repellence properties, PFAs have found use in many industries such as food packaging and textile. Recent studies report drinking water as one of the most common ways in which humans are exposed to PFAs [2]. As such, their detection and quantification in water is critical. Molecularly imprinted polymers (MIPs) are synthetic polymers possessing specific cavities designed for target molecules. They offer the advantage of selectivity, chemical tunability, high stability, mechanical strength, and ease of regeneration [3]. MIPs will be synthesized from β -cyclodextrin and activated carbon. Preliminary results show that activated carbon with a higher surface area ($2.0493 \text{ m}^2/\text{g}$) can be obtained using H_2O_2 as an oxidizing agent. Upon realizing the need for easy recovery after an application, magnetic nanoparticles were prepared and successfully incorporated into the tea waste activated carbon (TWAC) as observed from the FTIR. From the Raman spectrum, the D and G bands of activated carbon could be identified in both the TWAC spectrum and the magnetized TWAC, indicating successful modification. Further characterization with X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), and Thermogravimetric Analysis (TGA) will be conducted. The synthesized materials will be used to prepare MIPs and applied for extracting various PFAs in water.

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GREEN SYNTHESIS OF TiO₂ NANOPARTICLES USING TEA EXTRACT AND THEIR PHOTOCATALYTIC ACTIVITIES

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Over the last two decades, oxide nanostructures have been continuously evaluated and used in many technological application : electronic, environment and nanomedicine with various other important applications such as pharmaceuticals, nuclear energy, fuel and energy, cosmetics, and biosensors. The advancement of the controlled synthesis approach to design desired morphology is a fundamental key to the discipline of material science and nanotechnology. These nanostructures can be prepared via different physical and chemical methods; however, a green and ecofriendly synthesis approach is a promising way to produce these nanostructures with desired properties with less risk of hazardous chemicals [1].

In the last years, titanium dioxide (TiO₂) nanoparticles have gained much importance because of their remarkable catalytic properties and distinctive semiconducting properties. TiO₂ is also a chemically stable, non-toxic and biocompatible material. They have emerged as promising photocatalysts for water purification [2].

The present research work focused on the synthesis of Titanium dioxide (TiO₂) nanoparticles from Tea leave extract using Green synthesis process. The Tea leaf extract was prepared by the maceration extraction method and the synthesis of TiO₂ NPs was obtained using an adequate protocol followed by calcination and activation at different temperatures 400°C, 500°C and 600°C. The synthesized TiO₂ nanoparticles were characterized by several techniques such as X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-VIS) and Attenuated total reflection infrared (ATR-IR).

A photocatalytic study of TiO₂ nanoparticles synthesized at different temperatures 400°C, 500°C and 600°C was tested in the photocatalytic degradation of methylene blue (MB) dye. The results obtained showed a better removal of MB dye with TiO₂ NPs synthesized at 600°C. This application of green TiO₂ nanoparticles is being explored for further development in the context for wastewater treatment applications.

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Electro photocatalytic degradation of organic pollutants over Ce doped-CaTiO₃ nano-perovskite.

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Effective energy development and environmental protection play a significant role in sustainable development [1]. The increase in population growth and, increase in consumption of fossil fuels have led to major environmental pollution issues and public health concerns. Therefore, development of cost-effective solutions devoted to removing organic pollutants mostly in water and converting carbon dioxide and nitrogen in the atmosphere have attracted the attention of researchers' [2]. Perovskite materials are promising candidates particularly in the field of photocatalysis, pollutant degradation and other applications such as energy conversion etc. due to their numerous properties such as high absorption, high mobility and high diffusion length of charger carriers which are beneficial factors in degradation of organic pollutants [3]. The approach used during synthesis of perovskites affects how green or environmentally friendly the prepared material will be rated [4]. Perovskite-based material represent the fast-advancing scientific technology in terms of energy-conversion. This is the next generation low cost, high-performance and sustainable energy technology [5]. In this project Ce doped-CaTiO₃ nano-perovskite materials will be synthesised and tested for their photoelectrochemical properties of the degradation of methylene blue in water.

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Impacts of sodium bicarbonate and co-amine monomers on properties of thin-film composite membrane for water treatment

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Polyamide (PA) thin-film composite (TFC) nanofiltration (NF) membranes are widely used for the treatment of water and wastewater treatment. However, the membrane surface properties could be further modified during interfacial polymerization (IP) process to achieve higher water flux and salt rejection. Herein, the effects of sodium bicarbonate (NaHCO_3) and co-amine monomer—2-(2' aminoethoxy) ethylamine (AEE) on the characteristics of piperazine (PIP)-based TFC membranes were investigated for water purification and aerobically treated palm oil mill effluent (AT-POME) treatment. Characterizations based on field emission scanning electron microscopy (FESEM), Fourier transform infrared analysis (FTIR) and contact angle were carried out to provide support to the filtration results. Results showed that 0.5 wt% NaHCO_3 Was the best loading to be added to improve the membrane performance by enhancing water permeability by 37% without affecting Na_2SO_4 rejection. In the presence of 0.5 wt% NaHCO_3 , it is found that the introduction of AEE into PIP solution could further improve the Na_2SO_4 rejection of PIP-based membrane from 97.1 to 98.5% while producing a permeate of better quality. Further evaluation using AT-POME indicated that the AEE-modified membrane was able to enhance the separation performance of PIP-based membrane, increasing its conductivity, colour (ADMI) and COD reduction from 74.31, 92.79 and 83.4%, respectively, to 79.15, 94.26 and 89.3%. This work demonstrates the positive features of using inorganic additive and secondary amine monomer in improving characteristics of TFC membrane for water and wastewater treatment.

Keywords: Thin-film composite membrane, Monomer, Salt rejection, Polyamide, Nanofiltration, AT-POME, Antifouling

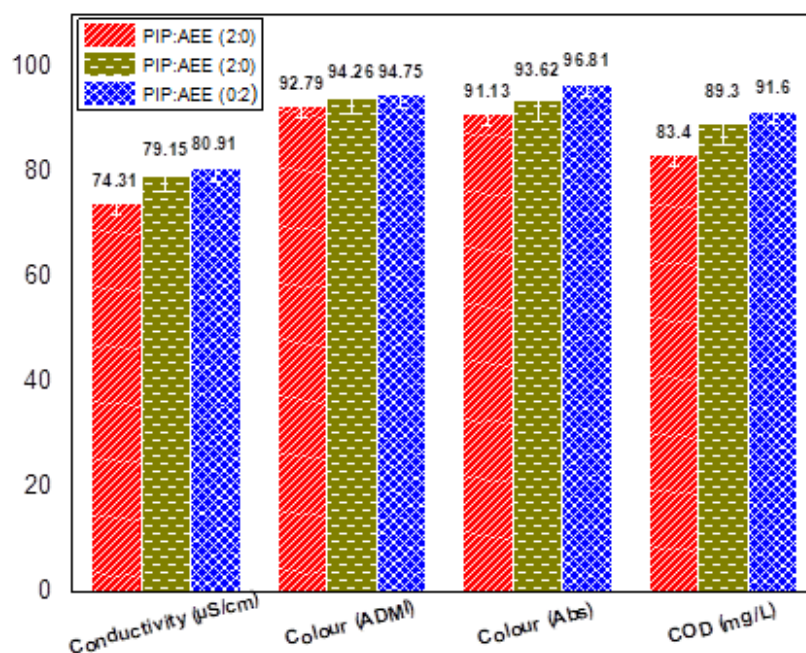


Figure 1: Separation performances of different TFC membranes for AT-POME treatment

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Synthesis, DNA Base-Binding Properties and Anti-Oxidant Capabilities of Tetraaza Macrocyclic Ligand and it's Ni Complex

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A novel of 1-10 Phenathroline-based macrocyclic ligand (compound A) and its nickel complex (compound B) were synthesized by the condensation and complexation reactions respectively. The synthesized compounds were structurally verified by IR, ¹H NMR, ¹³C NMR, HPLC and Thermogravimetric analysis (TGA). The antitumor activity of the synthesized compounds were evaluated through DNA and GC-rich Amplicon binding assays and antioxidative assays. Their binding capabilities were monitored using UV/Vis spectrophotometer, PCR, and Gel Electrophoresis. The compounds had good DNA-Drug binding activities suggesting superior DNA intercalation and external binding capable of inhibiting PCR amplification of the DNA. Compounds A and B interactions with the GC-rich Amplicon showed better binding constants of 6.195x10⁻⁶ M and 2.335 x10⁻⁶ M respectively compared with their interactions with cf-DNA. The negative binding constants of compounds A (- 5.47x10⁻⁶ M⁻¹) and B (-1.87x10⁻⁶ M⁻¹) with cf-DNA suggested a favoured dissociation in their interactions over association. More so, the hypsochromic shift observed in Amplicon-compound B interactions revealed a possible reduction in the conjugation system of compound B. Differential thermal analysis showed that they all have higher thermal stability. These compounds can help in regulating cell function by modulating transcription and/or interfere with cell replication and DNA repair processes.

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Synthesis of Chitosan/Ag₃PO₄/PtCl₆²⁻ as Photocatalyst for Methyl Orange Degradation

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Ag₃PO₄ photocatalyst is a photocatalyst that is active in visible light because it has small bandgap energy. This study aims to determine the effect of composite formation with chitosan and platinum complexes dopant on Ag₃PO₄ on the photodegradation ability of methyl orange dye. Chitosan/Ag₃PO₄/PtCl₆²⁻ composites were successfully synthesized by coprecipitation method using AgNO₃, Na₂HPO₄·12H₂O, chitosan, and H₂PtCl₆·6H₂O. The results of the synthesis have been characterized using Fourier Transform Infra-Red which shows peak shift due to the addition of chitosan, X-Ray Diffraction which shows high crystallinity and has a body-centered cubic structure and Diffuse Reflectance Spectroscopy which shows an increase in bandgap energy to 3.33 eV. Chitosan/Ag₃PO₄/PtCl₆²⁻ photocatalyst has higher photocatalytic activity than Ag₃PO₄, but lower than Ag₃PO₄/PtCl₆²⁻ with the rate constants of Ag₃PO₄, Ag₃PO₄/PtCl₆²⁻, and Chitosan/Ag₃PO₄/PtCl₆²⁻ respectively 0.0267; 0.2056, and 0.103 min⁻¹. Chitosan/Ag₃PO₄/PtCl₆²⁻ photocatalyst has low stability with rate constants from reusable 1 to reusable 3, namely 0.134; 0.0511; and 0.0266 min⁻¹. Oxygen radicals (•O₂⁻) have a major role compared to other ROS in the process of photodegradation mechanisms that occur.

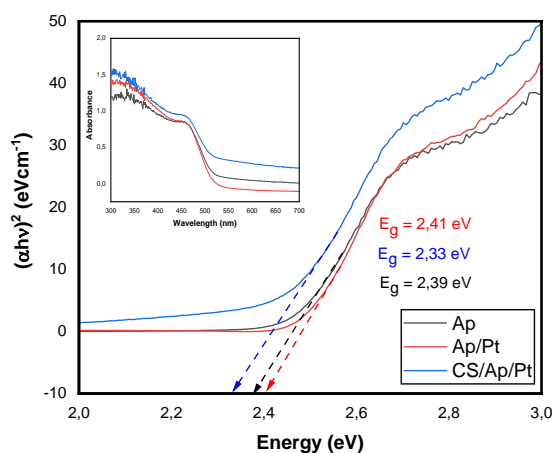


Figure 3. DRS Characterization of Ap (Ag₃PO₄), Ap/Pt (Ag₃PO₄/PtCl₆²⁻), and CS/Ap/Pt (Chitosan/Ag₃PO₄/PtCl₆²⁻)

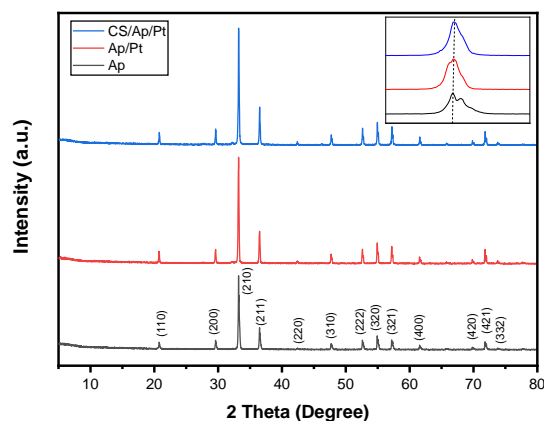


Figure 4. XRD Characterization of Photocatalysts

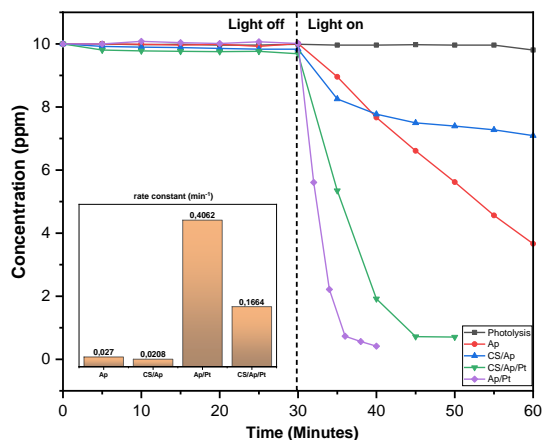


Figure 5. Photocatalytic Activity of Photocatalysts

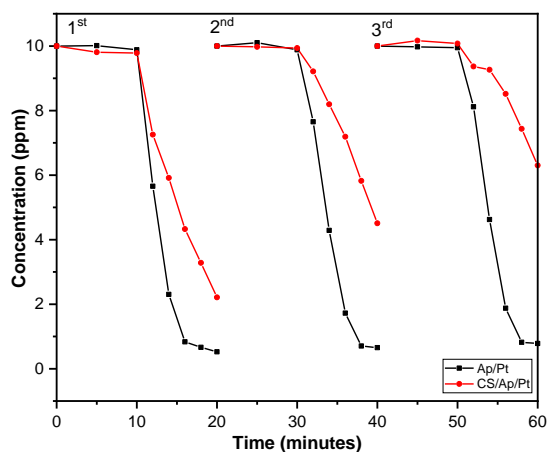


Figure 6. Reusability Evaluation of Photocatalysts

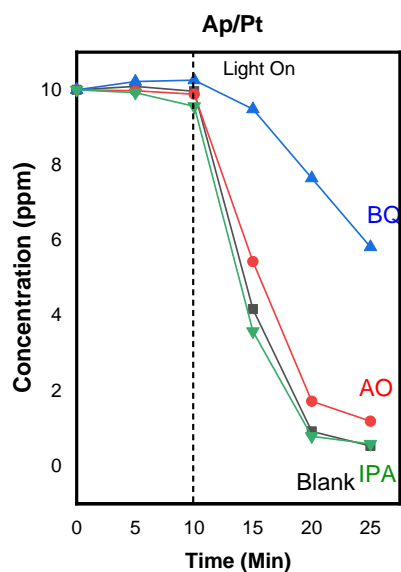


Figure 7. Mechanism Evaluation of Ap/Pt activity using ammonium oxalate (AO), isopropyl alcohol (IPA), and benzoquinone (BQ) as a scavenger

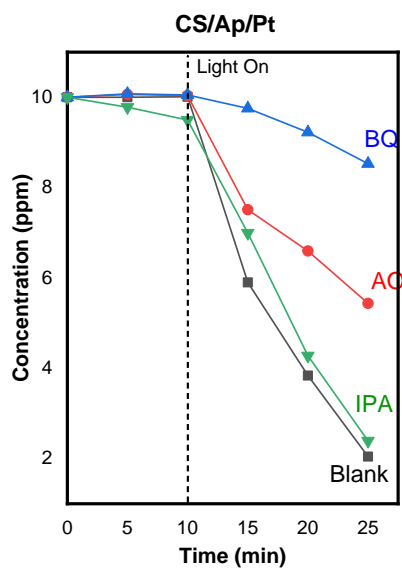


Figure 8 Mechanism Evaluation of CS/Ap/Pt activity using ammonium oxalate (AO), isopropyl alcohol (IPA), and benzoquinone (BQ) as a scavenger

Adsorptive removal of methylene blue dye using biodegradable superabsorbent polymer hydrogel composite incorporated with activated charcoal as adsorbent

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Hydrogels have attracted large attention in wastewater treatment due to their low-cost and good interaction with pollutants. Superabsorbent polymers (SAP) are the class of polymeric hydrogels that are cross-linked systems having a unique ability to imbibe water a hundred times their dried weight. Due to their extraordinary water retention ability with excellent hydrophilic properties, high swelling ratio, biocompatibility, and abundance in availability, they are also referred to as good adsorbents. Herein, superabsorbent polymer (SAP) hydrogels and their composite were prepared, with the incorporation of activated charcoal (SAP-AC) for the deep removal of an eco-toxic organic dye such as methylene blue (MB). The swelling ratio of the desired SAP was evaluated in a beaker containing 100 mg of SAP and 300 mL of ultra-pure (Milli-Q[®]) water at room (25 ± 2 °C) temperature. SAP showed maximum water retention capacity of 578 ± 7 g g⁻¹ (grams of water absorbed per gram of dry polymer) and SAP-AC showed 470 ± 4 g g⁻¹ respectively. A column was mounted and the adsorption parameters were optimized using an experimental Doehlert uniform array design for two variables (temperature, pH). A continuous up-flow fixed-bed column with an internal flow rate of 28 mL/min was fed with 300 mL of MB (50 ppm) using a peristaltic pump. About 70 mg of dried composite adsorbent was immersed in the glass tubular reactor with a 6 cm internal diameter and 30 cm in length. The adsorption reaction was maintained for 24 h time duration and a small sample aliquot (5 mL) was collected at definite time intervals and was analyzed using a UV-Vis. spectrophotometer ($\lambda_{\text{max}} = 665$ 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. After 24 h time interval, MB adsorption capacity reached 194.48 mg g⁻¹ (96.96 MB adsorption) using SAP and 207.37 mg g⁻¹ (98.27% MB adsorption) using SAP-AC as adsorbent. To identify the time for reaching adsorption equilibrium and to understand the mechanisms of the adsorption process, the data were fitted with pseudo first-order and pseudo second-order models. According to the data plotted, pseudo second-order kinetics model best fitted the data, and the experimental value for maximum MB adsorption capacity “ q_m ” was nearly equal to the calculated one. The experimental data were further applied to the Langmuir and Freundlich isotherms to determine MB adsorption behavior. Fitting the data to the Freundlich isotherm produced a higher R^2 , suggesting that the adsorption of MB on the hydrogel was multilayer adsorption. According to the SEM analysis, the SAP composites have a wrinkled and porous texture. From the XRD analysis of the SAP composites, it was deduced that the SAP material is comprised of amorphous nature. The current study has proved that the synthesized superabsorbent polymer composites have the good activity and selectivity for the deep adsorption of MB dye.

Boron complexes of dipyrromethenes, BODIPYs

Victoria Eirini Glypti

Boron complexes of dipyrromethenes, BODIPYs, were discovered from Treibs and Kreuzer in 1968. From then, many more derivatives have been found, and their study is becoming more and more essential. Their properties and applications are endless, which can be seen from the growing interest these compounds have held in the last decades. BODIPYs are considered very prominent compounds for their use in many fields. These fields include chemistry, biochemistry, biology, biotechnology, along with medicine and clinical diagnosis. BODIPYs are excellent fluorescent compounds, and they can usually emit light from the UV spectrum into the visible and near-IR spectrum wavelength.

Furthermore, they hold numerous properties such as high fluorescent quantum yields Φ_F , high molar extinction coefficients ϵ , solubility in various organic solvents. They can be easily functionalized by introducing different groups in the BODIPY core. Their research is also vital due to their use as biological labels and probes, photovoltaic devices, light-emitting devices, and photodynamic therapy.

The aim of this research project was to synthesize different BODIPY derivatives and a starting material, 2-ethylpyrrole. So, in this research project, boron complexes of dipyrromethenes were produced from pyrroles and acid chlorides. In total, five BODIPYs were made in a multi-step reaction. To analyze the BODIPYs, methods like NMR, MS, IR and UV-Vis were used. Their yields were moderate, ranging from 7-15 %.

Synthesis and Activity of Photocatalyst Composite defect- $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{PtCl}_6^-$ For Degradation of Rhodamine B Dyes and Antibacterial Agents

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Ag_3PO_4 are photocatalysts active in visible light because they have small bandgap energy. This study goal to analysis the effect of crystal defects and the formation of composites with $\text{g-C}_3\text{N}_4$ and platinum dopant on the synthesis of photocatalysts based on Ag_3PO_4 for the degradation of Rhodamine B dye and the antibacterial agent of *Staphylococcus aureus*. The defect- $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{PtCl}_6^-$ was successfully synthesized by the co-precipitation method using the precursors AgNO_3 , $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\text{g-C}_3\text{N}_4$, and H_2PtCl_6 . Formation of defect- $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{PtCl}_6^-$ proved to increase photocatalytic activity in the degradation of Rhodamine B dye and antibacterial activity against *Staphylococcus aureus*. Photocatalyst defect- $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{PtCl}_6^-$ has better photodegradation ability than other materials with a photodegradation rate constant of 0.2575 min^{-1} . Antibacterial activity was tested by diffusion method and results showed that the defect- $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{PtCl}_6^-$ had higher antibacterial activity than other photocatalyst at a concentration of 1,000 ppm. The enhancement of photodegradation ability and antibacterial activity was due to the synergistic effect between the defect, composite to $\text{g-C}_3\text{N}_4$, and PtCl_6^- dopant.

Table 1. Rate constant of Rhodamine B photodegradation[1]

Sample	Photodegradation Rate Constant (min^{-1})
Ap	0,0915
D-Ap	0,1347
D-Ap/CN	0,15
D-Ap/Pt	0,1923
D-Ap/CN/Pt	0,2575

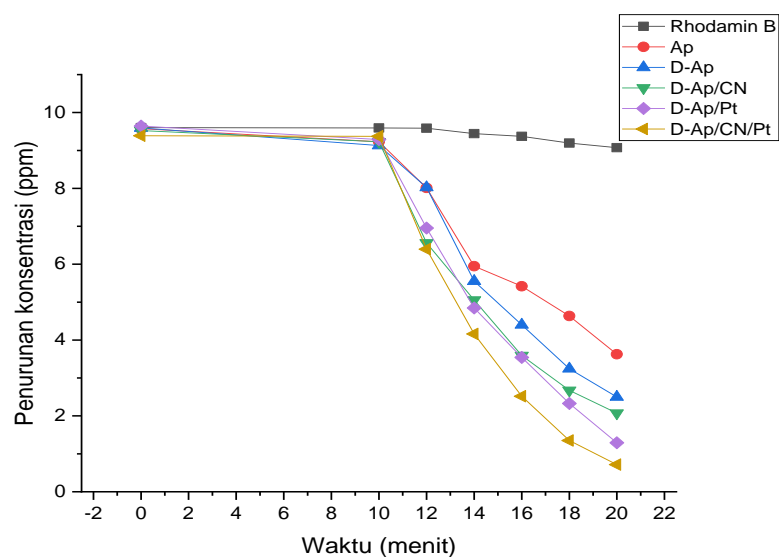


Figure 1. Photodegradation activity towards Rhodamine B

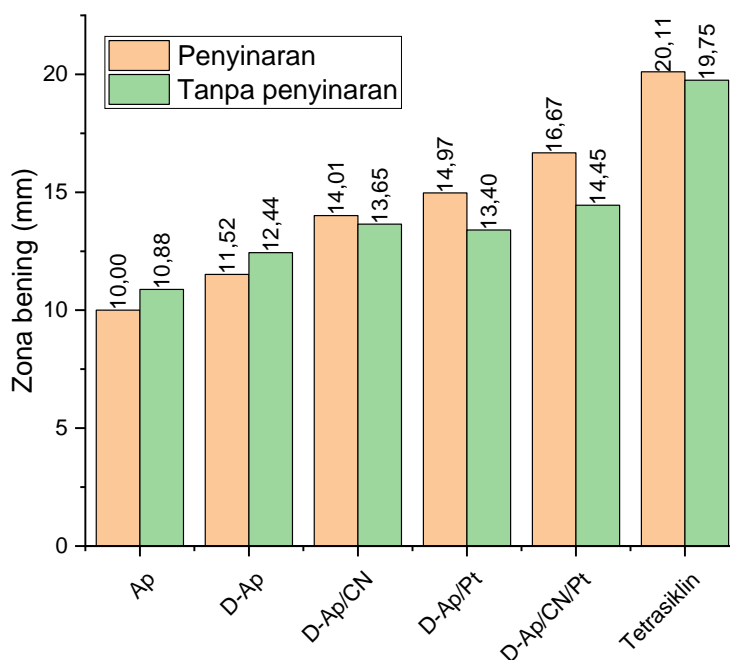


Figure 2. Antibacterial activity of composite photocatalyst towards *Staphylococcus aureus*[2]

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5. FOOD SAFETY

GREEN SYTHESIZED NANOPARTICLES AS PLANT NUTRUENT SUPPLEMENT

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Farmers all around the world strive to employ soil rich in nutrients to produce enough and high-quality crops to feed the world's ever-increasing population. Soil nutrient deficiency is caused by an unbalanced utilization of nutrients in the soil. Micronutrient deficiency has an impact on human health as well as plant development. Plants cultivated in nutrient-deficient soil create nutrient-deficient food, which affects people who rely on these foods for nutrient. Farming practices has resulted in a 50-70 percent loss of micronutrient. Nanotechnology-based smart method can help conventional farmer become more sustainable. This research aimed to evaluate the potential of Zinc-nanoparticles as micronutrient. The sol-gel method was used to synthesize ZnO nanoparticles. The synthesized Zn nanoparticles were characterized using SEM, UV, FTIR, XRD. Soil was collected from the university premises and characterized with XRF, therefore were treated with zinc oxide nanoparticles in proportions of 0%, 25%, 50%, 75% and 100%, before tomato planting. The results revealed a larger number of leaves and tomato height than control with 75% treatment having the highest yield. Conclusively, application of zinc should be at adequate concentration for the plant to obtain efficient growth and plant yield and it is recommended that the application of Zinc nanoparticles should be encouraged in subsistence and commercial agriculture and it help to retain soil fertility.

Novel microspheres based on alginate/chitosan- nanocomposites as delivery vehicles of omega-3 rich oils

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Novel microspheres based on alginate/chitosan- nanocomposites were prepared to reduce omega-3-rich oils oxidation and to obtain the maximum health benefit. The investigated fish or flaxseed oils with nano-clay have been nanoemulsified with and without curcumin (Cur) as a natural antioxidant and followed by their incorporation into crosslinked polymeric microspheres. The microspheres were developed from alginate (AL), chitosan (CS), and their combination (ALCS). Oxidative stability, microencapsulation efficiency, and the oil release rate, in addition to antioxidant and antibacterial actions, were examined. The results of DLS data of nanocomposites and Cur-loaded nanocomposites showed somewhat larger but still acceptable particle sizes ranging from 139-153 nm and zeta potentials ranging between -2.02 and -3.51 mV. The entrapment of fish or flaxseed oils in the developed microspheres was confirmed by FTIR and XRD. Optical microscopy, stereo microscopy, SEM, and AFM demonstrated that microspheres had a spherical shape. Cur improved microencapsulation efficiency, loading capacity, and thermal stability of the microspheres. AL-based microspheres suffered a significant increase in oil oxidation than CS and ALCS microspheres. It was generally noted that the addition of Cur enhances and retards the oil oxidation of the formulated microspheres. *In vitro* release profile at neutral medium showed a better-sustained release than at acidic medium. The results suggested that the microspheres could be applied as effective and safe vehicles for omega-3-rich oils with broad-spectrum antibacterial activity. Also, the obtained results suggested the suitability of the formulated nanocomposites-loaded microspheres to be used in food and pharmaceuticals products oils.

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PRECISION IN SHOATS SELECTION USING TELOMERES

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Time wastage in the farm due to 'unseen' genetic and health disorders contributes to economic losses and high levels of methane, this occurs due to unprecise selection criteria. The heritable nature, correlation between lifespan, genetic diseases to telomere length is of great impact to the selection of suitable sheep in early life stages. Sheep and goat telomere length is heritable making it a possible parameter for selection. Telomeres are protective structures at the end of chromosomes that maintain the integrity of the genome by ensuring that chromosomes are not recognised as sites of DNA damage. This study followed the telomere measurement guidelines as described by Cawthon, 2002. We conducted two separate PCRs simultaneously, a Telomere PCR and a Single copy gene (beta-2-microglobulin (B2M) PCR for all samples. This was as such in order to get the ratio between the two as the average telomere length is usually presented as the amount of single copy gene which is a constant to the amount of telomeric DNA. B2M was used as it has been previously used in soay sheep and freshian cattle telomere dynamics experiments and has shown stable qPCR results.

The fluorescence thresholds were different across all samples. The single gene copy had an average of 2.081 while the TEL gene had an average of 2.123. The lengths are shorter for animals with lower growth rates, lower milk production, more disease manifestations and more reproductive disorders like abortions. The telomeres are longer for animals described to have a better quality life.

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Interpolyelectrolyte complexes based on polydiallyldimethylammonium chloride and sodium polystyrenesulfonate as a potential material for creating safe for health and effective antibacterial coatings for food safety

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In some areas, such as food industry, there are high requirements for sanitary standards. Biofilms formed on the wall surfaces in food production and storage rooms and the multiplication of bacteria on the surfaces of food transport and processing equipment can lead to food contamination and subsequent severe food poisoning. Recently, polymers have been widely used as functional coatings, including coatings with antibacterial properties. It is necessary to single out a class of polycations that carry a positive charge in each monomer unit, which facilitates their interaction with negatively charged bacterial membranes. One of these polycations is polydiallyldimethylammonium chloride (PDADMAC), used as the flocculant for water treatment, which has been shown to possess antimicrobial activity. To increase the adhesion of PDADMAC to various surfaces, it is necessary to modify it with hydrophobic blocks. Such a modification can be achieved through the formation of an interpolyelectrolyte complex (IPEC) with a polyanion, for example, sodium polystyrenesulfonate (PSS). It should be noted that PDADMAC and PSS are approved by the FDA for medical use, also such biocides could be applied from the aqueous phase, which means that there is no need to use organic solvents that can be allergens for humans or animals, as well as pollute the environment. In this work, we studied the properties of water-soluble IPECs based on PDADMAC and PSS, the effect of increasing the share of PSS in the complex on antibacterial activity, and the possibility of forming coatings based on IPEC.

The interaction of PDADMAC with PSS was studied by turbidimetric titration of a PDADMAC solution. It has been established that water-soluble IPECs can be obtained at ratios of anionic and cationic groups in the composition of polymers $\chi = [\text{PSS}]/[\text{PDADMAC}]$ up to a critical value of 0.16. It is known that IPEC solutions are capable of undergoing phase separation when the ionic strength of the solution changes. The behavior of water-soluble IPECs with compositions less than critical was studied in various solutions of salts of mono- and bi-valent ions. It has been established that all the studied complexes are resistant to phase separation in a wide range of ionic strengths of solutions.

To confirm the feasibility of further studies, it is necessary to evaluate the biocidal activity of PDADMAC and its water-soluble IPECs with PSS. First, screening for antimicrobial activity with reporter-system was carried out. The result was compared with a similar experiment for two antibiotics, levofloxacin (Lev) and erythromycin (Ery). Due to the use of a double reporter bacterial system pDualRep2, it was revealed that PDADMAC and IPECs have similar red halo like Ery, and, probably, affect the stage of protein biosynthesis. For the polycation and its IPECs the minimum inhibitory concentrations were also determined, at which there is a complete suppression of the growth of bacteria of several cultures, using Ery as a control. PDADMAC was found to exhibit more effective antimicrobial activity against Gram-positive *B. subtilis* than Gram-negative *E. coli* *dTolC KanR*. It is important that IPECs also retain biocidal activity with an increase in the proportion of PSS.

The coatings from PDADMAC and IPEC were obtained by applying a solution to the hydrophilic and hydrophobic surfaces, and the resistance of the resulting coatings to wash off was studied gravimetrically. Polycation and IPECs were shown to form thin films on the hydrophilic and hydrophobic surfaces. It was found that IPEC films retained on the any substrate even after 6 wash-off cycles, while PDADMAC films stopped registering gravimetrically after 4 cycles. The coatings were visualized by atomic force microscopy. It was found that after the same wash cycle, the average film thickness of the IPEC coating exceeded the average thickness of the polycationic coating. Thus, it was shown that the hydrophobization of PDADMAC with PSS increases the resistance to washing off of coatings formed from its water-soluble complex from hydrophilic and hydrophobic surfaces.

Taking into account the described properties and the fact that PDADMAC and IPECs demonstrated an antimicrobial effect, and in addition, have the potential to create a polymer matrix that includes traditional low molecular weight biocides, it can be concluded that the studied IPECs is a potential material for creating antibacterial coatings.

Acknowledgements

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6. CLIMATE CHANGE

Assessing circular processes using new tool of NCCPCT

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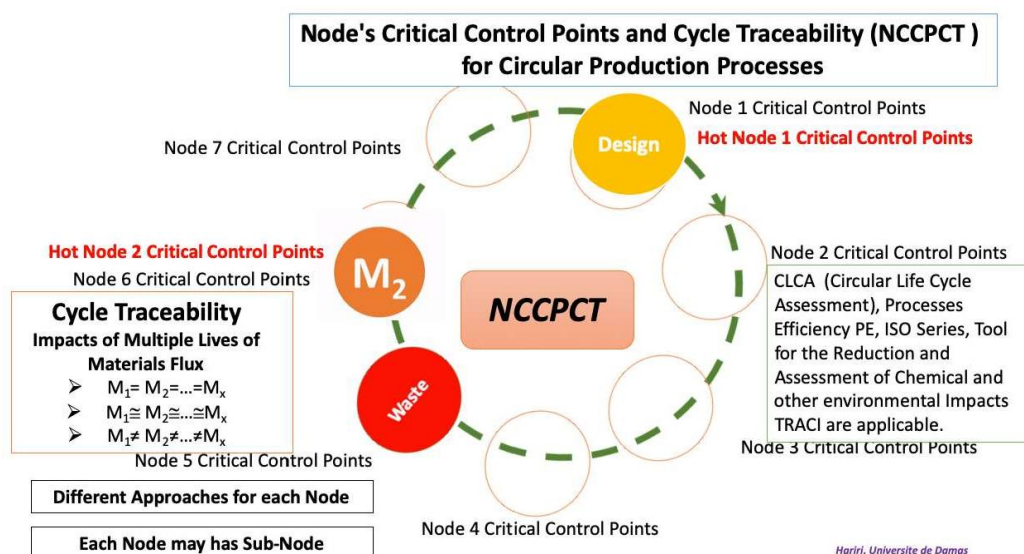
Depending on the revision of classical environmental and industrial risks assessments tools of the linear industrial processes (PRA, HAZOP and Bowtie) and analyzing main differences between Circular and Linear production processes, the new tool of Node's Critical Control Points and Cycle Traceability (NCCPCT) for Circular Production Processes was developed, examined and applied preliminary in three different typical contexts such as polymers, water and mineral circularity.

The tool divides the whole circular processes to sub-processes and considering each one as a node.

Multi-criteria methods were adopted according to the characterization of the processes in each node. Detection of work atmospheric carbon dioxide gas using laser techniques were introduced for industrial processes monitoring.

An applicable interactive diagram of the NCCPCT has been drawn for preliminary assessment of main Circular Processes to accord wide range of different typical contexts of circularity.

The limitations of multiple lives of material were introduced through simulation software to offer reliable results of characterization degrading in the quality of fluxes. Significant risks have been identified as hot nodes or fluxes to be indicators for further preliminary environmental and safety measures.



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The role of C-scorpionate metal complexes for the conversion of CO₂

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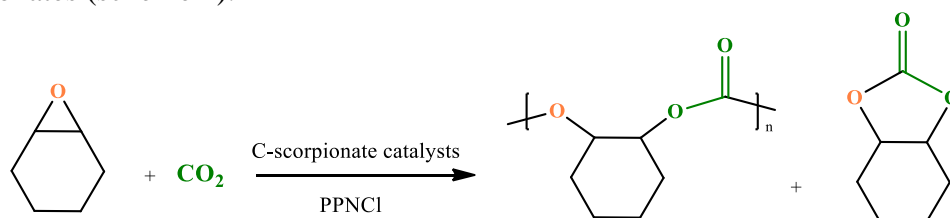
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Nowadays society is being confronted with one of the most challenging problems of all, the mitigation of greenhouse gases. The main cause of global warming and ocean acidification is due to anthropogenic emissions of CO₂ released from industries. Therefore, it is important to develop fully functional catalytic systems that mitigate this problem by converting CO₂ into fuels and commodities.

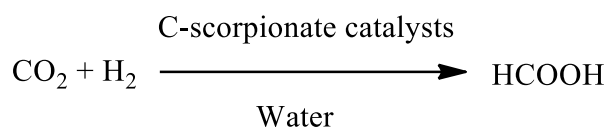
Herein, we report the successful use of two different C-scorpionate metal complexes as catalysts applied for CO₂ conversion, to afford:

i) polycarbonates (scheme 1):



Scheme 1. Solvent free copolymerization of CO₂ with cyclohexene oxide catalysed by a C-scorpionate catalyst.

ii) formic acid (scheme 2):



Scheme 2. Single pot conversion of CO₂ with H₂ catalysed by a C-scorpionate catalyst.

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INNOVATIVE PROCESSES FOR RECYCLING MULTICOMPONENT PACKAGING MATERIALS

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Multicomponent packaging materials are widely diffused in food industry thanks to their high performances in terms of mechanical, optical and barrier properties, resulting from the combination of functionalities of different materials (**Figure 1**). This allows a prolonged products shelf-life and relatively low costs. However, conventional waste management systems are not adapted to identify, sort and recycle multilayered materials.

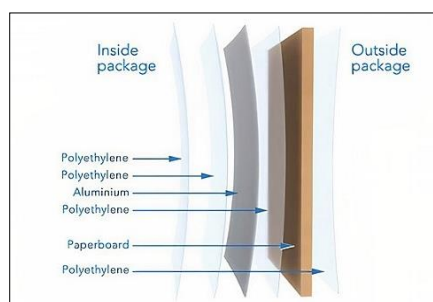


Figure 1. Structure and composition of a typical multicomponent packaging material.

The aim of this project is to develop innovative and effective methods for the recycling of metalized multicomponent materials. The recovery of the highest amount of material is targeted as well as the possibility to re-use each recovered component separately. Exploitation of green methods is also a major goal.

The processes developed in this work consist in the use of alternative solvents (such as biodiesel, anionic surfactants, switchable hydrophilicity solvents) for the solubilization or delamination of the polymeric layer, allowing its separation from the metal. All the described methods showed satisfying results (**Table 1**) regarding the recovery of polymeric material, metal and solvent, thus establishing this research project in a context of circular economy. Moreover, several studies on the retrieved components highlighted the remarkable purity of both the polymer and the Al, consequently ensuring the efficiency of the recycling technique.

Future goals would be the extension of these processes to other types of multicomponent packaging materials, the scale-up of these methods and the use of other substances (commercial or synthetic) as solvents.

METHOD	MASS BALANCE	Al PURITY ^a	SOLVENT RECOVERY
<i>Biodiesel^b</i>	100%	99%	99%
<i>Surfactants^b</i>	99%	98%	98%
<i>SHS^c</i>	95%	97%	85%

^a in terms of contamination, obtained from SEM analysis of Al surface;

^b PE-based samples; ^c PP-based samples.

Table 2. Results about the recovered materials.

DEVELOPMENT OF NEW HOMOGENOUS CATALYSTS FOR CO₂ REDUCTION TO FORMATES.

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The huge consumption of fossil resources and the resulting CO₂ 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 C₁ source which is non-toxic, non-flammable and non-corrosive. The utilization of CO₂ requires high energy hence catalysts are required to overcome kinetic and thermodynamic stability.[4, 5, 7] The heterogenous hydrogenation of CO₂ 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).

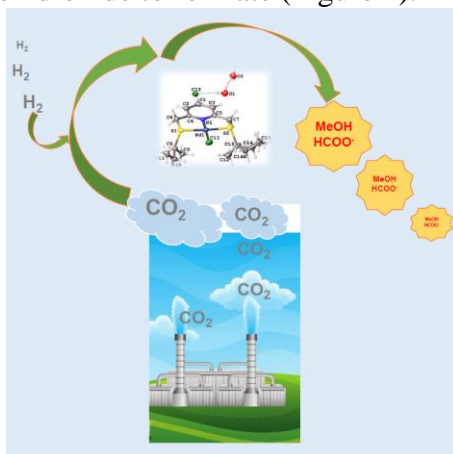


Figure 1: Illustration of CO₂ hydrogenation to formate.

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Design and synthesis of novel Lanthanide based metal-organic frameworks (MOFs) for catalytic hydrogenation of carbon dioxide to formic acid

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Increased levels of atmospheric carbon dioxide (CO₂) are a global concern, prompting scientists to find ways of utilizing CO₂ to produce useful chemicals and clean energy sources.¹ The currently used fossil fuels are the primary cause of the dramatic increase of CO₂ amounts in the atmosphere.² Hence there is a need for new clean energy sources with minimal pollution hazards.

Formic acid is one of the products that can be obtained from CO₂ hydrogenation.³ Formic acid represents a convenient hydrogen carrier in fuel cells making it a value-added chemical for use in the hydrogen energy storage front.⁴ It is noted that formic acid has an energy content that is at least five times greater than commercially available lithium ion batteries.⁵ Sustainable chemical technologies can make use of the CO₂ pollutant to produce useful chemicals whilst saving the environment.

Metal-organic frameworks (MOFs) have tunable synthesis, with a choice organic linker and metal center, robust materials can be produced and these have found a wide range of applications including catalysis.⁶ Lanthanide based MOFs possess solvothermal stability as the Lanthanide and oxygen bond is superior to any other metal and oxygen bond aiding the robustness of these materials.

Our research findings indicate that Lanthanide based MOFs can be synthesized over a wide range of temperatures and possess catalytic properties, as they can convert CO₂ to formic acid. Improved catalytic properties are seen when the MOFs are functionalized with platinum group metal complexes such as Pt(II),⁷ Ir(III),⁸ Ru(II),⁹ Pd(II),¹⁰ and Rh(III),¹¹ Lanthanide based MOFs are promising catalysis candidates for CO₂ utilization, producing formic acid which is a great alternative for hydrogen energy storage.

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Primary, Secondary, and Tertiary sewage sludge pyrolysis for sustainable energy

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Sewage sludge has become a major environmental challenge because it is produced on a large scale and still has uncertain final destination. In this work, the primary (PS), secondary (SS) and tertiary (TS) sludge were pyrolyzed at 450°C. SS and TS show similarities in volatile matter (73.44/72.8%), fixed carbon (9.31/7.19%), ash (17.25/19.95%), calorific value (18.70/18.48 MJ.kg⁻¹), combustibility ratio (0.13 / 0.10) and O/C fraction (0.49/ 0.50). PS has a high ash content both in the raw sludge and in the biochar (35.26% and 59.96%). XRF/EDX data reveal the absence of potentially toxic metals in all samples. PS, has a higher concentration of alkali and alkaline earth metals (K=2.78 mg.kg⁻¹, Ca and Mg= 3.34 and 2.68 mg.kg⁻¹, respectively), Fe/Al/Si (Fe= 5.56 mg.kg⁻¹, Al=4.95 mg.kg⁻¹, Si=6.70 mg.kg⁻¹) and phosphorus (P=6.54 mg.kg⁻¹). The combustion profiles demonstrate that the devolatilization stage of the raw sludge occurred between 148–391°C and that of the biochars between 215–416 °C, due to the combustion of volatile matter, organic debris and bacteria. The conversion rate of PS, SS and TS was 6.76, 6.00 and 5.85 %·min⁻¹, respectively, while the solid yield of PSB, SSB and TSB showed the lowest loss, 4.53, 6.09 and 7.96% respectively. There is greater reactivity of raw sludge (SS>TS>PS) than of biochars (PSB>TSB>SSB). Biochars have lower ignition performance, burnout efficiency and combustibility index than raw sludge, but are more stable during combustion and have properties similar to coal. The oil and fat content of PS is 4%, of SS 2.5%. Infrared Spectroscopy and Nuclear Magnetic Resonance of ¹³C and ¹H of all bio-oils and oils indicate the presence of carbon sp³, sp², and carbonyl groups referring to carboxylic acids.

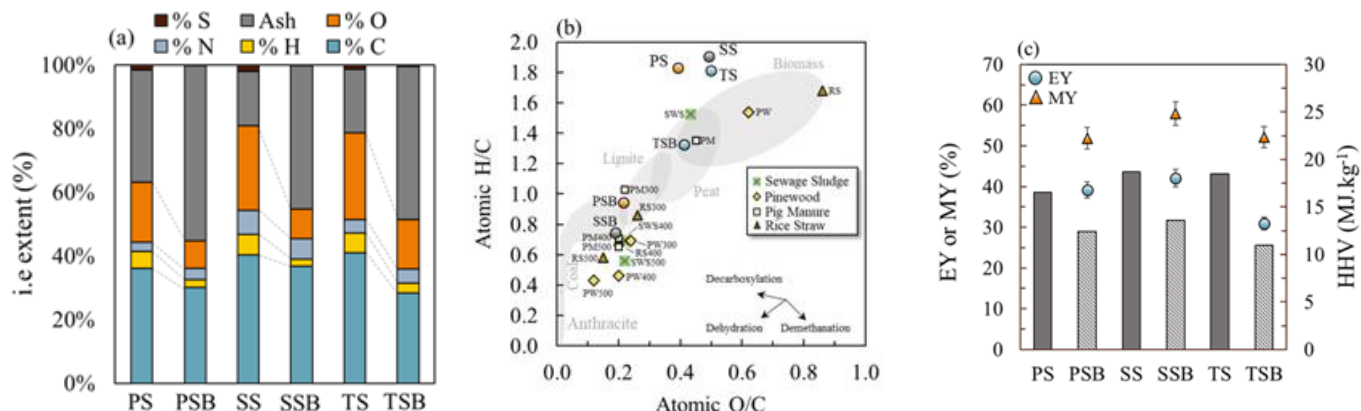


Figure 9- (a) Ultimate composition, (b) Van Krevelen diagram, (c) SY, EY, and HHV, for raw (SS, PS, and TS) and biochar products (PSB, SSB, and TSB)

Biopolymeric Based Electrochemical Cell for the Removal and Recycling of Toxic Solvents from Pharmaceutical Effluents

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Keywords: AOPs, Electro-degradation, Adsorption, VOCs, AOX, MOS biosorbents, GC-FID.

Volatile organic compounds (VOCs) are recalcitrant highly toxic contaminants regularly found in pharmaceutical effluents [1]. The ongoing challenge is that pharmaceutical pollutants cannot be effectively removed by conventional wastewater treatment plants (WWTPs) because of the inadequacy of the unit processes [1]. The biological treatment process such as activated carbon filtration, ozonation and hydrodynamic activation also do not seem to remove these solvents because they are miscible with water. Consequently, a vigorous, selective, and rapid abatement method are required for the removal of VOCs in wastewater streams. In this study, electrochemical degradation of three VOCs (benzene, toluene and ethylbenzene: BTE), 300 mM each, was investigated by coupling of an indirect anodic oxidation (IO) in the presence of modified nickel foam (Ni@MMOxNWs) as working anode followed by adsorption of by-products using *Moringa Oleifera* seed biosorbents. The adsorbable organic compounds (AOX), chlorine species (Cl⁻) and nickel species (Ni²⁺) were also monitored simultaneously. A rapid, selective, and precise GC-FID method was developed and validated for analysis of the VOCs in synthetic wastewater samples for both techniques. The VOCs calibration plot showed a coefficient R²>0.9960 for targeted compounds (BTE). The evaluation of the VOCs removal was done using modified Ni foam wafer (9.12 cm² surface area) as working and graphite plate as cathode in the presence of 2500 m/L NaCl as supporting electrolyte, 300μM initial VOCs concentration and current density of 2.30 mA/cm² and low energy consumption of 0.063 kWh/g of pollutant. The electro-treated effluent samples underwent possible AOX biosorption using various MOS sorbents. The electro-degradation of VOCs was successful showing removal efficiencies of > 90% for all VOCs, the COD removals of > 50% and TOC removal of > 60% for electro-degradation process that were further reduced by sorption. The removal of possible AOX compounds revealed that all compounds were beyond detection limit. As a result, the Ni sludge produced during the electro-degradation was completely removed by MOS sorbents in the trend Ac-MOS>D-MOS and R-MOS, respectively.

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will be optimized. The employ of large nickel particles (> 6 wt % Ni) favor the cracking reactions, reducing the yield of the reaction.

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Thermal exploitation strategies for paper mill waste

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One of the main problems of our society is the high generation of wastes that are currently discharged to landfill, causing environmental and economic issues [1-2]. On this basis, from a circular economy perspective, it is urgent the development of sustainable strategies for valorizing these materials. In this context, the papermaking industry produces a large amount of inorganic-rich sludges which, at the moment, are exploited for agricultural application, for energy recovery and/or for the production of bio-composites [3]. However, the above possibilities do not valorize each fraction of the starting feedstock, which includes inorganic and organic components, opening the way towards more promising strategies of fractionation and exploitation.

In this perspective, the present investigation studied thermal treatments for the fractionation of inorganic sludges. The aim of this study is the recovery of the calcium carbonate, the main component of the inorganic sludge, that could be reused as filler in different materials [3]. First of all, a chemical characterization of the inorganic sludge has been performed and successively a pyrolysis approach has been developed. This is a thermochemical process where the feedstock is converted/fractionated under nitrogen atmosphere to give a liquid bio-oil, a solid biochar and non-condensable gases. The achieved results have been compared with those obtained by a simpler combustion treatment carried out at 400°C for 4 hours. Finally, a preliminary characterization of all the recovered fractions from the thermal approaches has been performed in order to propose their valorization within the context of a more sustainable and integrated process.

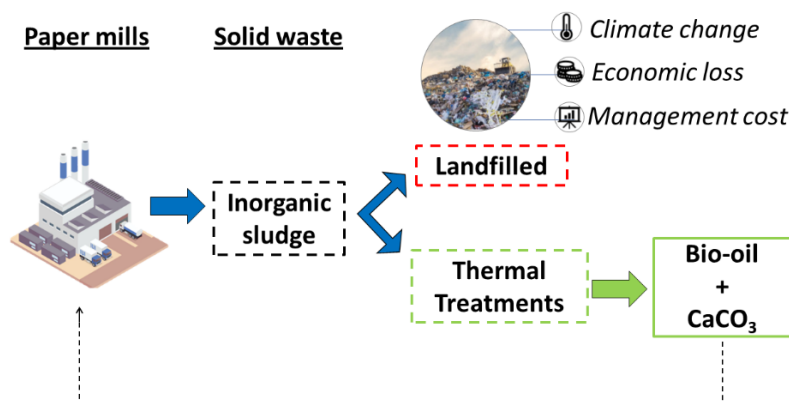


Figure 1. Proposed strategies for the exploitation of industrial paper mill waste.

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Nanostructured Cu-based Catalysts Electrochemically Synthesized on a Carbonaceous Gas Diffusion Layer for CO₂ Electroreduction

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Global warming caused by the increase of the carbon dioxide in the atmosphere is considered one of the most serious problems to which human being must find a solution. Despite the mitigation policies introduced in many industrialised countries, the need to reduce its concentration is, now more than ever, urgent [1]. In this scenario, the electrochemical reduction of carbon dioxide (CO₂ER) to high added-value chemicals is becoming particularly attractive due to its clean and mild operative conditions combined with the renewable energies [2]. Among all the different metals suitable for this approach, Cu has been acknowledged as the only one capable to reduce the CO₂ toward >C₂ products [3].

In this work, we present a comparative study of the catalytic performances of a set of electrosynthesized Cu⁰ nanostructured films coupled with different copper oxide species supported on carbonaceous gas diffusion membranes, tuning the morphologies and the redox active couples in order to find out the most active one [4]. The electrocatalytic performances were evaluated in a H-type cell (Figure 1a) filled with 0.3 M KHCO₃ and containing Ag/AgCl (saturated KCl) and a Pt gauze as reference and counter electrodes, respectively, both placed in the opposite side of that containing the working electrode to facilitate the next future transition to catholyte-less conditions. A Nafion membrane was used in between. As a result (Figure 1b), all the oxidized electrocatalysts showed a selectivity toward the acetic acid production at -0.4 V vs RHE and, in particular, the one based on the Cu⁺/Cu⁰ redox couple turned out to be the most active catalyst, displaying the highest acetic acid productivity (308 μmol g_{cat}⁻¹ h⁻¹) and a Faradaic Efficiency (FE) of 76%.

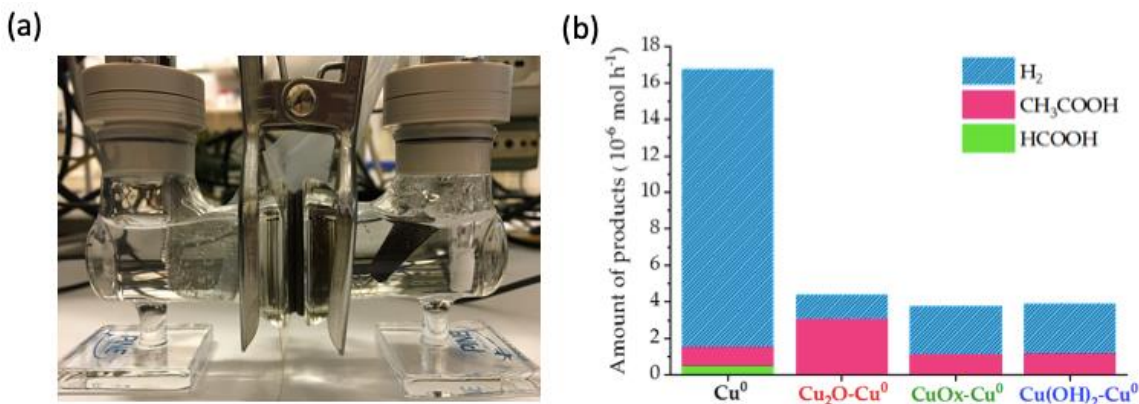


Figure 1. (a) H-type cell; (b) products distribution at -0.4 V vs RHE, 1h reaction

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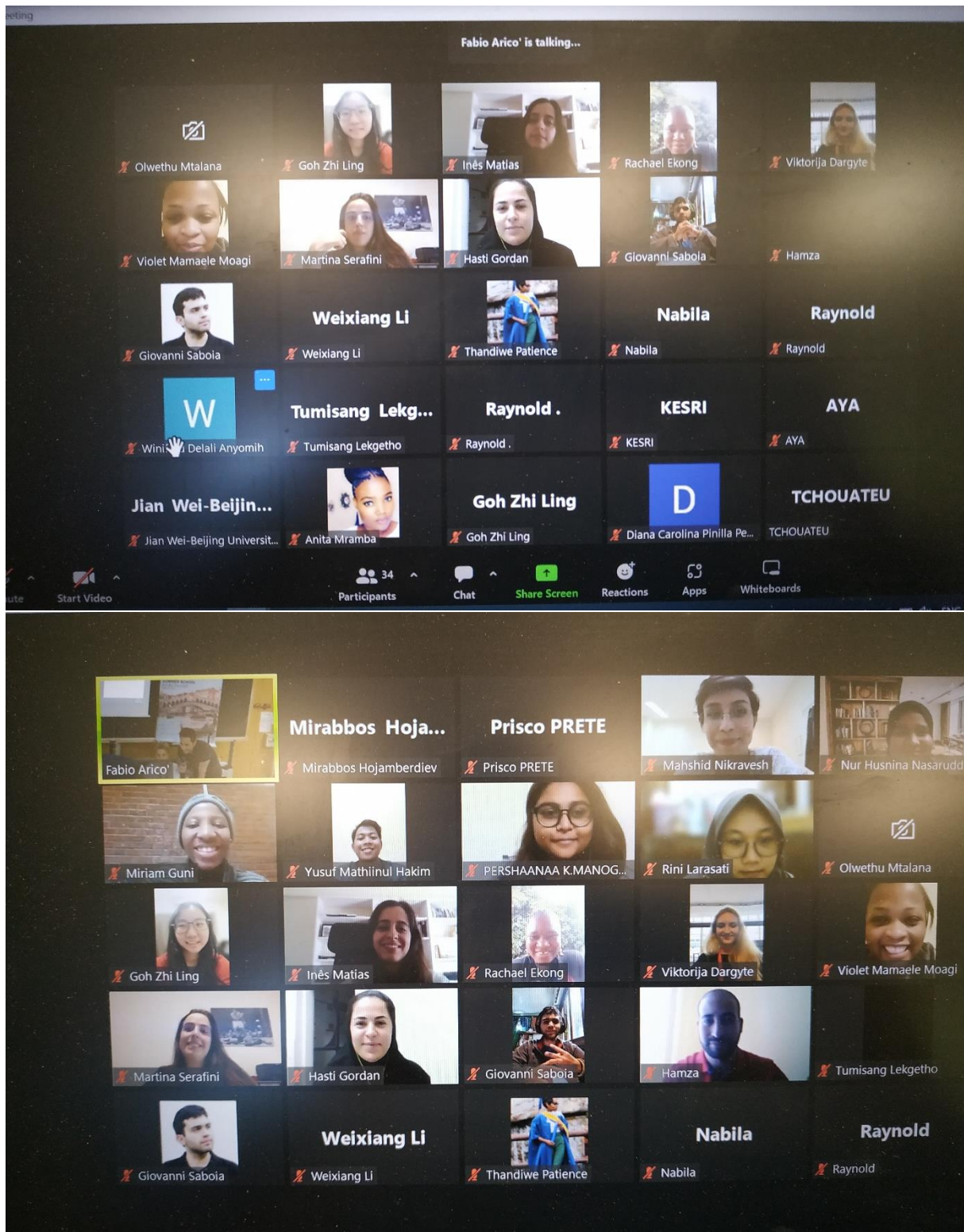
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