

JULY 7-13, 2018 – VENICE



**Green Chemistry**

**IUPAC Postgraduate Summer School**

7th-14th July 2018 Venezia, Italy

# **GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL**

**7-14 July 2018**

**Palazzo Ducale**

**Cultural Center Don Orione Artigianelli**

**Venice, Italy**



**Sustainability through Green Chemistry**

JULY 7-13, 2018 – VENICE

**IUPAC Postgraduate Summer School on Green Chemistry  
7-13 July 2018, Venice – Italy**

**Book of Abstracts**

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**JULY 7-13, 2018 – VENICE**

## **WELCOME MESSAGE FROM THE CHAIR OF THE SUMMER SCHOOL**



Dear Colleagues,

It is with a great pleasure that I welcome you in Venice for the IUPAC Postgraduate Summer School on Green Chemistry which for the first time is carried out under the IUPAC Interdivisional Committee on Green Chemistry for Sustainable Development umbrella.

It is a great achievement that about half of the postgraduate students attending the School (about 80 in total) come from developing countries and have been awarded with a scholarship of €500 each.

So many grants were possible thanks, in addition to IUPAC Divisions and Committees, to the generous participations of the sponsors: Eni, L'Oréal, PhosAgro and the Organization for the Prohibition of Chemical Weapons.

I would like to thank here IUPAC President Prof. Qi-Feng Zhou, and Vice-President Prof. Christopher Brett who will be with us during the Summer School.

I would like to thank also my colleagues of the IUPAC Italian National Committee for their support.

My particular thanks go to Prof. Peter Licence, co-editor of *ACS Sustainable Chemistry & Engineering* for the opportunity of publishing the best contributions of the School on ACS Journal.

The Summer School main topics are:

- Renewables & Green Energy
- New Reaction Pathways
- Green Materials
- Reaction Media
- Analytical Chemistry & Green Chemistry for Restoration

The Summer School has obtained the endorsement of the European Year of Cultural Heritage 2018 and the choice of Venice as Host city for the Summer School has offered the opportunity to highlight the emerging connection of Green Chemistry with cultural heritage restoration and conservation field. In fact, Monday 9th July at Palazzo Ducale will be especially dedicated to restoration of cultural heritage goods through green chemistry with the participation of important experts in the field, also in collaboration with Venice Superintendence.

Students will have the opportunity to expose their research and work at the Summer School Poster Session and the best posters will be rewarded by the Sponsors at the awarding ceremony at Palazzo Ducale on Friday 13<sup>th</sup> July.

I wish all of you to be in the future key persons in your respective countries, thus contributing to the pacific development of chemistry and its results all over the world.

The Summer School will be the occasion for you to exchange ideas and make friendship with colleagues at an international level, and we will do our utmost to ensure that these links and connections are permanent also in the future!

I invite all participants to actively participate with their suggestions and ideas during the Summer School with hope that closer connections are established also for the future.

**Pietro Tundo**  
*Chairman, Organizing committee*

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## **WELCOME MESSAGE FROM THE IUPAC PRESIDENT**



As the president of IUPAC, I feel honored to present at the first IUPAC Postgraduate Summer School on Green Chemistry.

IUPAC experts has been working on Green Chemistry mainly through a Subcommittee for many years. During Prof. Natalia Tarasova's Presidency, with the efforts of Prof. Pietro Tundo and many others, the previous Subcommittee grew into a new Interdivisional Committee of Green Chemistry for Sustainable Development, aiming to bring all the Union Bodies' devotions in this field together, as well as to emphasize our orientation to 17 UN-Goals.

This Summer School, as a project of the new Interdivisional Committee, aims to facilitate the exchange of information and ideas of Green Chemistry. Welcome all the participants! For lecturers from various backgrounds, thank you for sharing your valuable research contributions. For students, I hope you will find this six-day experience highly helpful with your further research in this field. Then I would like to thank our organizers and all the supporters to make all this happen, especially the Italian hosts who brought their precious experiences from previous successful Summer Schools. My thanks also goes to sponsors of this summer school and PhosAgro who generously sponsored the PhosAgro/UNESCO/IUPAC research grants in green chemistry. Participations of the industrial sector are crucial for the accomplishment of the sustainable development goals.

In the end, I wish this Summer School all the success! IUPAC will celebrate its Centenary in 2019, and one important project is the next Postgraduate Summer School on Green Chemistry to be held in Africa. I hope participants coming here today will continue to give us your support on this series of projects and the development of Green Chemistry in general!

**Qi-Feng Zhou**  
*IUPAC President*

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## **SUMMER SCHOOL COMMITTEES**

### **CHAIR OF THE SUMMER SCHOOL**

- **Pietro Tundo:** Università Ca' Foscari di Venezia – Venice, Italy

### **LOCAL ORGANIZING COMMITTEE**

- **Fabio Aricò:** Università Ca' Foscari, Venice, Italy
- **Elena Griguol:** Università Ca' Foscari, Venice, Italy
- **Pietro Tundo:** Università Ca' Foscari, Venice, Italy
- **Andrea Vavasori:** Università Ca' Foscari, Venice, Italy

### **SCIENTIFIC COMMITTEE JURY**

- **Jan Apotheker:** University of Groningen, Netherlands
- **Fabio Aricò:** Università Ca' Foscari, Venice, Italy
- **Chris Brett:** University of Coimbra, Portugal
- **Christine Luscombe :** University of Washington, Seattle, USA
- **Janet Scott:** University of Bath, UK
- **Pietro Tundo:** Università Ca' Foscari, Venice, Italy
- **Angela Wilson:** Michigan State University, USA

### **PROJECT TASK GROUP MEMBERS**

IUPAC Project N° 2017-006-2-041

- **Jan Labuda:** Slovak University of Technology in Bratislava, Slovakia
- **Mehmet Mahramanlioglu:** İstanbul Üniversitesi, İstanbul, Turkey
- **Supawan Tantayanon:** Chulalongkorn University, Thailand

### **WEB MANAGER**

- **Stefano Bonetta:** Università Ca' Foscari, Venice, Italy
- **Elena Griguol:** Università Ca' Foscari, Venice, Italy

### **DATABASE MANAGER**

- **Roberto Dallochio:** CNR Istituto di Chimica Biomolecolare – Sassari, Italy

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**LECTURES & TEACHERS**  
(alphabetical order)

**FABIO ARICÒ**

Associate Professor of Organic Chemistry, Ca' Foscari University of Venice, Italy  
**Dialkyl Carbonates and Bio-Based Platform Chemicals**

**ROBERTO BALLINI**

University of Camerino, Italy  
**One-pot Synthesis of a Variety of Target from Aliphatic Nitro Compounds**

**CHRISTOPHER BRETT**

Department of Chemistry, Faculty of Sciences and Technology, University of Coimbra, Portugal  
**Electrochemistry and green chemistry: from deep eutectic solvents to corrosion protection**

**CINZIA CHIAPPE**

FRSC Department of Pharmacy, University of Pisa, Italy  
**Ionic liquids: Twenty years of research to dispel myths and establish facts**

**HOWARD M. COLQUHOUN**

Chair of Materials Chemistry, Department of Chemistry, University of Reading, UK  
**Materials chemistry of the fuel cell: a clean and sustainable energy-technology.**

**ALBERTO FIGOLI**

Institute on Membrane Technology (ITM-CNR), Rende (CS), Italy  
**Green Chemistry in Membrane Science and Technology**

**JONATHAN FORMAN**

Science Policy Adviser at the Organisation for the Prohibition of Chemical Weapons (OPCW)  
**Sustainability and Disarmament: how Green Chemistry Contributes to WMD Security**

**NICHOLAS GATHERGOOD**

ERA Chair of Green Chemistry, Division of Chemistry, Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology, Estonia  
**The Design Of Safer Chemicals: Are Mineralisable Compounds An Achievable Goal?**

**MICHAEL GRAETZEL**

Director of Photonics and Interfaces (LPI), Institute of Chemical Science and Engineering Faculty of Basic Science Ecole Polytechnique Federale de Lausanne, Switzerland  
**Light and energy, mesoscopic photosystems mimic photosynthesis**

**JULY 7-13, 2018 – VENICE**

**WOLFGANG F. HOELDERICH**

President of TCHK Chemical Technology and Heterogeneous Catalysis, Frankenthal, Germany  
**Renewable Feedstocks for Environmentally Friend and Sustainable Chemistry**

**KLAUS KÜMMERER**

Director of the Institute of Sustainable and Environmental Chemistry (University of Lüneburg, Germany) and Scientific Director of Research and Education at the International Sustainable Chemistry Collaborative Centre (ISC3, Bonn, Germany)  
**Benign by Design-Designing Materials, Chemicals and Pharmaceuticals for Sustainability**

**JAN LABUDA**

Institute of Analytical Chemistry, Faculty of Chemical and Food Technology  
Slovak University of Technology in Bratislava, Slovakia  
**Approaches of Analytical Chemistry Reflecting Principles of Sustainable Chemistry**

**PETER LICENCE**

Associate Professor, University of Nottingham, UK

**SIROJ LOIKOV**

Deputy Director General for International Projects, PhosAgro, Russia  
**PhosAgro is a stimulus to progress in green chemistry through the grant programme Green Chemistry for Life.**

**RAFAEL LUQUE**

Departamento de Química Organica, Universidad de Cordoba, Spain  
**Waste-to-wealth: biomass and waste to valuable chemicals, materials and fuels using green chemical technologies**

**MEHMET MAHRAMANLIOGLU**

İstanbul Üniversitesi Mühendislik Fakültesi Kimya Bölümü - Avcılar – İstanbul, Turkey  
**The green approach to energy in Turkey**

**ROCCO MAZZEO**

Full professor of Chemistry for Cultural Heritage and Head the Microchemistry and Microscopy Art Diagnostic Laboratory of the University of Bologna, Italy  
**Materials and methods for the conservation of works of art. From current practice towards a green attitude in art conservation: new bio-based organogels for the cleaning of bronzes and paintings.**

**COSTANZA MILIANI**

Institute of Molecular Science and Technologies (CNR-ISTM, Perugia - ITALY).  
Senior research scientist and coordinator of the European facility MOLAB.  
**Non invasive spectroanalytical methods for a sustainable diagnostic in heritage science**

**EGID B. MUBOFU**

Vice Chancellor, University of Dodoma (UDOM), Tanzania

**Standardization for sustainable development**

**MICHEL PHILIPPE**

L'OREAL Fellow Sustainable Innovation Manager L'OREAL R&I International Raw Material Department, France

**Green Chemistry to innovate sustainably**

**GIACOMO RISPOLI**

Executive Vice President of Portfolio Management & Supply and Licensing Department - Eni Refining & Marketing, Italy

**Biorefineries and Green Diesel: process and product innovation**

**EUGENE V. ROZANOV**

PMOD/WRC, IAC ETHZ, KF IZMIRAN, Switzerland

**Is there any danger to ozone layer recovery in the future?**

**SANSONETTI ANTONIO**

Institute for Conservation and valorization of Cultural Heritage National Research Council - Milan

**Green chemistry at the service of Conservation: cleaning artworks with gels**

**JANET L. SCOTT**

Department of Chemistry, Centre for Doctoral Training in Sustainable Chemical Technologies, University of Bath, UK

**Designing and manufacturing materials with appropriate lifetimes – materials to fit with the circular economy**

**MASSIMO TRANI**

Vice President for Proprietary Technology Licensing department at Eni, Italy

**Eni Advanced Biofuels**

**PIETRO TUNDO**

Professor of Organic Chemistry, Ca' Foscari University of Venice, Italy

**The Chemistry of Dimethyl Carbonate**

**ALEXEY A. ZANIN**

UNESCO Chair in Green Chemistry for Sustainable Development Dmitry Mendeleev University of Chemical Technology of Russia, Russia

**Ionic Liquids – Green Solvents or Not?**

**QI-FENG ZHOU**

College of Chemistry and Molecule Engineering, Peking University, China

IUPAC President

**CHAIRMEN**

**SUNDAY 8 JULY MORNING**

2<sup>nd</sup> SESSION: Pietro Tundo

**SUNDAY 8 JULY AFTERNOON**

1<sup>st</sup> SESSION: Fabio Aricò

2<sup>nd</sup> SESSION: Nicholas Gathergood

**MONDAY 9 JULY MORNING**

1<sup>st</sup> SESSION: Elisabetta Zendri

2<sup>nd</sup> SESSION: Francesco Trovò

**MONDAY 9 JULY AFTERNOON**

1<sup>st</sup> SESSION: Roberto Ballini

2<sup>nd</sup> SESSION: Egid Mubofu

**TUESDAY 10 JULY MORNING**

1<sup>st</sup> SESSION: Jan Labuda

2<sup>nd</sup> SESSION: Rafael Luque

**TUESDAY 10 JULY AFTERNOON**

1<sup>st</sup> SESSION: Howard Colquhoun

2<sup>nd</sup> SESSION: Klaus Kümmerer

**WEDNESDAY 11 JULY MORNING**

1<sup>st</sup> SESSION: Wolfgang Hoelderich

2<sup>nd</sup> SESSION: Mehmet Mahramanlioglu

**THURSDAY 12 JULY MORNING**

1<sup>st</sup> SESSION: Pietro Tundo

2<sup>nd</sup> SESSION: Christopher Brett

**THURSDAY 12 JULY AFTERNOON**

1<sup>st</sup> SESSION: Alberto Figoli

2<sup>nd</sup> SESSION: Cinzia Chiappe

**FRIDAY 13 JULY MORNING**

1<sup>st</sup> SESSION: Janet Scott/Jonathan Forman

**JULY 7-13, 2018 – VENICE**

**SUMMER SCHOOL TOPICS**

**Renewables & Green Energy**

**New Reaction Pathways**

**Green Materials**

**Reaction Media**

**Analytical Chemistry & Green Chemistry for Restoration**

## TEACHERS' LECTURE ABSTRACTS

### EUGENE V. ROZANOV

PMOD/WRC, IAC ETHZ, KF IZMIRAN, Switzerland

#### **Is there any danger to ozone layer recovery in the future?**

Montreal Protocol and its Amendments (MPA), which limit the production of halogen containing ozone depleting substances (hODS) were introduced in 1997 after the discovery of the ozone hole and global total column ozone (TCO) decline. The efficiency of MPA was confirmed by the observed decrease of some halogen containing species, ozone recovery in the upper stratosphere and robust ozone layer recovery in the future simulated with state-of-the-art chemistry-climate models. On the other hand, the ozone hole in the Southern hemisphere is still very deep and persistent negative ozone trend in the lower stratosphere over middle and low latitudes did not stop in 1998. The absence of this trend in the model simulations suggests that some unaccounted processes or forcing factors are missing in the state-of-the-art models. In this lecture talk I will review the main processes responsible for the ozone layer variability and discuss potential influence of the solar activity decline, greenhouse gases and some newly discovered chemical species as well as potential new limitations aimed at the sustainable future ozone recovery.

## RENEWABLES & GREEN ENERGY

### MICHAEL GRAETZEL

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

#### **Light and energy, mesoscopic photosystems mimic photosynthesis**

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] as light harvesters have emerged as credible contenders to conventional silicon cells photovoltaic devices. Separating light absorption from charge carrier transport dye sensitized mesoscopic solar cells (DSCs) were the first to use a three-dimensional nanocrystalline junction for solar electricity production [1]. The conversion efficiency for DSC's is currently 14-15 % and over 22.7 % for perovskite pigments. 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, the industrial production of DSC's attaining presently the multi-MW/year scale. The fundamentally new concepts have been applied to realize the solar generation of hydrogen from water by photo-electrochemical cells [6] as well as the combination of perovskite solar cells with water electrolyzers [7]. The current research status of this field will be presented

#### **References:**

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- [3] M. Grätzel, *Nature* 414, (2001) 338.
- [4] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, Md.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel *Science* 334 (2011) 629
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**LOIKOV SIROJ**

*Deputy Director General for International Projects, PhosAgro, Russia*

**PhosAgro is a stimulus to progress in green chemistry through the grant programme Green Chemistry for Life.**

Nowadays green chemistry has become a target for cutting-edge research into sustainable technologies. These technologies may reduce or eliminate the production and use of hazardous substances in mining, manufacture and application of chemical products, and may also lead to energy saving and a better environment and health.

Research in green chemistry and allied areas in biochemistry, geochemistry, biotechnology, ecology and healthcare give young scientists ample opportunity to demonstrate their inventiveness and provide important input to sustainable development.

With this in mind, the Green Chemistry for Life Project was launched in 2013 by UNESCO's International Basic Sciences Programme and PhosAgro, the largest producer of phosphate-based fertilizer globally, in close cooperation with the International Union of Pure and Applied Chemistry.

**RAFAEL LUQUE**

*Departamento de Química Organica, Universidad de Cordoba, Spain*

**Waste-to-wealth: biomass and waste to valuable chemicals, materials and fuels using green chemical technologies**

**Keywords:** Green Chemistry, Nanomaterials design, Biomaterials, heterogeneous Catalysis, photocatalysis, biocatalysis, Flow Chemistry, biomass valorisation, waste valorisation, biorefineries

The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years. Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials, designer nanomaterials for catalytic applications and catalytic strategies for biomass/waste conversion into useful materials, chemicals and fuels have sustained the research portfolio of leading sustainability research Institutions worldwide in recent years. These topics have extensively covered, among others, the preparation and design of strategies and methodologies for a wide range of applications in biomass and waste valorisation practises.

In this lecture, we aim to provide an overview of recent (own) efforts and future prospects in research & innovation in sustainable biorefineries as a platform to lead the future of global scientists from chemical engineers to (bio)chemists, environmentalists and materials scientists.

**MEHMET MAHRAMANLIOGLU**

*İstanbul Üniversitesi Mühendislik Fakültesi Kimya Bölümü - Avcılar – İstanbul, Turkey*

**The green approach to energy in Turkey**

**Keywords:** renewable energy, barriers to green energy technologies, incentives for green energy technologies, green technologies in industry, green buildings, green cities.

Global warming threatens human life in our day. Governments, international organizations, non-governmental organizations, companies and universities are engaged in various activities against such a great danger that threatens the existence of human beings. Since the size of the danger is very well understood in our country, state, non-governmental organizations, universities are working on this issue.

In this presentation, we will discuss the activities related to reducing the use of fossil fuels and increasing the use of renewable energy in our country. Renewable energy power plants and projected power plants to be used in the future are being introduced

The presentation is based on three bases. 1-What the state does on this issue-2-What companies do on this issue 3-What the universities do about it.

It is also explained that non-governmental organizations are doing to enlighten the people on this subject

In the presentation, Turkey's nuclear energy, solar energy, wave energy and wind energy activities and activities on energy forestry are explained.

**MICHEL PHILIPPE**

*L'OREAL Fellow, Sustainable Innovation Manager, L'OREAL R&I, International Raw Material Department, France*

**Green Chemistry to innovate sustainably**

Sustainable innovation [1, 2] is a key-objective for L'Oréal Group which has soon integrated the principles of sustainable development into all stages of a product's life cycle, from its design to consumer use.

This fundamental goal is expressed by a clear and ambitious commitment: 100% of products have to bring an environmental or social benefit by 2020.

This objective will be reached in particular by using in our new formulas always more plant-origin ingredients originating from sustainable resources and compliant with the green chemistry principles.

The development of the green chemistry principles, initially proposed by P.T. Anastas and J.C. Warner [3] and integrated in the Group for more than 10 years from now [4] are strategic with the respect of 3 basic pillars:

- Use of renewable raw materials [5]
- Development of eco-respectful processes [6, 7]
- Innovation based on ingredients with favorable environmental impact [8].

Our determined objective is to constantly increase the volume of renewable ingredients in our numerous marketed formula. If the latter are transformed, we commit to use synthesis processes with the smallest environmental impact in compliance with the green chemistry principles.

It thus becomes vital to evaluate the origin and the process of extraction or/and transformation of each of the raw materials in our portfolio, knowing that these raw materials may contain one or several ingredients. This large-scale assessment enables us to have a thorough knowledge of their naturalness and their level of denaturation in order to increase the percentage of green chemistry raw materials.

It is proposed that the criterion of naturalness of a raw material is a component of an index linked to its origin and of a denaturation index linked to the level of transformation to which it is subjected between its origin and use [9]. The calculation of these indexes and their coherence with the new ISO 16128 standard on cosmetic natural ingredients recommending compliance with the green chemistry principles are described in details.

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**GIACOMO RISPOLI**

*Executive Vice President of Portfolio Management & Supply and Licensing Department - Eni Refining & Marketin, Italy*

**Biorefineries and Green Diesel: process and product innovation**

**JANET L. SCOTT**

*Department of Chemistry, Centre for Doctoral Training in Sustainable Chemical Technologies, University of Bath, UK*

**Designing and manufacturing materials with appropriate lifetimes – materials to fit with the circular economy**

As “molecular designers” chemists are able to design and produce a diverse range of polymers, fillers and coatings with distinct properties for specific purposes. These are used in industry to manufacture a very wide range of highly sophisticated products that may need to last for a long time, e.g. car parts and building materials, or that have short lifetimes and need to (bio)degrade post use, e.g. packaging and personal care products. In spite of the very different lifetime requirements and end-of-life fates of such materials we often use a small range of very robust and persistent polymers as the major component. In a truly Circular Economy approach, we should match the lifetime and end-of-life fate of materials and take this into account in the design stage asking the following questions, amongst many others:

1. Will the material be recovered and recycled many times? If so, we need it to be robust and must avoid contamination that frustrates recovery and remanufacture.
2. Will the material be a “single-use” and then be discarded to landfill or waste-water treatment plant? If so, we need it to be stable on the shelf until it is used, but to degrade readily to innocuous products when it is discarded.

In addition to these issues, we must also consider the source of the raw material (is it made from fossil carbon or from a renewable source), its production (is the process “clean and green”) and its function (does it do what we need it to do)? These topics will be discussed using specific case studies to demonstrate that more sustainable materials can be devised if we start with appropriate design principles that include sustainability and fit with the circular economy.

**MASSIMO TRANI**

*Vice President for Proprietary Technology Licensing department at Eni, Italy*

**Eni Advanced Biofuels**

To counteract the overcapacity of refining that has occurred in Europe since the years of the recent economic crisis, with the risk of closing the less profitable refineries, Eni has developed and patented a conversion method from a traditional fossil refinery to a Biorefinery, that processes renewable vegetable charges in order to obtain high quality Greendiesel. This conversion, based on a proprietary technology called Ecofining™, has been implemented in the industrial sites of Venice and Gela, with the dual objective of avoiding the closure of the sites and thus safeguarding jobs, and of producing large quantities of Greendiesel and thus comply with the European obligation to place on the market up to 10% in place of fossil fuels.

The Biorefinery has a great operational flexibility with regard to raw materials that can be processed. However, there is a regulatory and environmental limit to the so called “first generation biofuels”, obtained from raw materials in competition with the food sector (eg sugary, starchy and oilseed crops).

A recent objective of the European directives is to increase the obligation and promote the introduction of “advanced biofuels” (from lignocellulosic biomasses, agricultural and forest waste, organic fraction of urban waste and aquatic biomass, raw glycerine, etc ...).

The waste oils and fats benefit from a bonus (double counting) as they are more sustainable, but are not considered "advanced", or with a high degree of sustainability.

To meet the requirements of the legislation it is therefore necessary to identify real "advanced" raw materials, compatible with the Ecofining process.

The paper provides an overview of current State of Art of Eni's research on advanced feedstocks, and on supporting circular economy initiatives.

## **NEW REACTION PATHWAYS**

### **FABIO ARICO'**

Associate Professor, Cà Foscari University, Venice, Italy

#### **Bio-based platform chemicals and dialkyl carbonates: synthesis, functionalization and applications**

In the last twenty years biorefinery has gained exceptional attention in the scientific community. This interest has been prompted by the substitution of petroleum-based compounds with renewable substances with the aim of establishing a bio-based economically self-sustained industry. In this prospect the US Department of Energy (DOE) has published a list of 10 target molecules, starting from 300 original candidates, that were considered of special interest for biorefinery development. Some examples are succinic, fumaric and malic acids, 3-hydroxypropionic acid, glucaric acid, levulinic acid; D-sorbitol, hydroxymethylfurfural (HMF) and so on. These compounds have been selected by taking into consideration numerous factors such as available processes, economics, industrial viability, size of markets and their possible employment as a platform for the production of 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 have 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 ethanol and glycerol, and hydroxymethylfurfural still occupies a top position as it encompasses all of the desired criteria for a bio-based platform compound.

This lecture will be focus upon two of the most investigated platform chemicals: isosorbide and HMF. Their synthesis and functionalization via green reagent and solvents, such as dialkyl carbonates, will be address. Actual and future applications will be discussed.

### **ROBERTO BALLINI**

*University of Camerino, Italy*

#### **One-pot Synthesis of a Variety of Target from Aliphatic Nitro Compounds**

The synthesis of complex molecules is traditionally performed by a chain of separate steps, each of which its own conditions, reagents, solvent and catalyst. After each reaction is complete, the solvent and waste are removed and discarded, and the intermediate product is separated and purified. However, it would be much more efficient if two or more bonds could be formed or two or more transformations could be realized in one or few synthetic sequences without isolating the intermediates. It is obvious that this type of reaction would allow the minimization of waste, making its management much easier since, compared to stepwise reactions, the amount of solvents, reagents, adsorbents and energy consumption as well as the amount of work would be dramatically decreased. Further, the one-pot process can drive the equilibrium of each reaction to the process to the desired direction. Thus, these processes would allow an ecologically and economically favorable production of chemicals.

In this context, aliphatic nitro compounds have demonstrated to be the key starting materials for the realizations of a variety of "one-pot" synthetic processes for the preparation of a number of target.

**HOWARD M. COLQUHOUN**

*Chair of Materials Chemistry, Department of Chemistry, University of Reading, UK*

**Materials chemistry of the fuel cell: a clean and sustainable energy-technology.**

Fuel cells convert fuels such as hydrogen or methanol directly to electrical energy by reaction with oxygen in an electrochemical cell. Unlike heat-engines, fuel cells are not limited in the efficiency of their conversion of chemical potential to energy, and hydrogen fuel cells are pollution-free in that their only by-product is water. A key component of most modern fuel cells is a very thin polymer membrane containing anionic groups that enable the transport of protons (but not electrons) from the anode to the cathode, and the lecture will focus on recent developments in polymer chemistry that enable fuel-cell membranes to operate successfully at high temperatures and under conditions of low humidity. The development and application of such membranes for hydrogen generation from renewable resources will also be discussed.

**JONATHAN FORMAN**

*Science Policy Adviser at the Organisation for the Prohibition of Chemical Weapons (OPCW)*

**Sustainability and Disarmament: how Green Chemistry Contributes to WMD Security**

Green chemistry represents an approach to scientific research and development that ultimately seeks to make the world a better place. Researchers develop chemicals and chemical processes that do not harm health or the environment, and are designed to reduce or eliminate the use and generation of hazardous substances. Reducing chemical hazards include the consideration of precursors, products, intermediates, waste streams and unintended by-products. Green chemistry embodies within it, the design of safer chemicals and processes, degradability as a key property of materials to avoid toxic waste, and inherently safer chemistry to reduce risk and impact of a chemical incident. The developments green chemistry support sustainable development goals and bring potential sustainability benefits into the process industry and consumer products.

Ensuring the safety of people and protecting the environment also act as guiding principles in sectors outside of scientific research and chemical manufacturing. The commonality of green chemistry with these other sectors that uphold the same aspirational goals provides opportunity for researchers in this field to bring benefits with impact beyond research and development in the chemical sciences.

One such overlap is with efforts to eliminate the use of chemicals as weapons, the overarching goal of the Chemical Weapons Convention, an international disarmament treaty, in force since 1997 in 192 of the World's nations (the "States Parties" of the Convention). The obligations under this international disarmament treaty include destruction of chemical weapon stockpiles, compliance with the obligations of the treaty under an international verification regime and the promotion of international cooperation amongst the States Parties. The treaty itself requires that States Parties "assign the highest priority to ensuring the safety of people and to protecting the environment" and they "cooperate as appropriate with other States Parties in this regard". This cooperation includes using chemistry for peaceful purposes, using chemistry to promote economic and technological development and for capacity building between States Parties. In effect, chemical weapon disarmament looks to use chemistry as a tool of diplomacy. Furthermore, any reduction in the accessibility of chemical hazards supports the goals of eliminating the use of chemicals as weapons, by simply reducing the potential for available chemicals to cause harm.

This lecture will introduce the Chemical Weapons Convention and its implementation, discussing where and how green chemistry supports international chemical disarmament and international diplomacy.

**WOLFGANG F. HOELDERICH**

*TCHK Chemical Technology and Heterogeneous Catalysis, Frankenthal, Germany*

**Renewable Feedstocks for Environmentally Friend and Sustainable Chemistry**

The annual total consumption of organic raw materials in Germany is about 19 million ton; 82 % are based on crude oil, 8% on natural gas, 2 % on coal as well as 8 % on renewable feedstock. These 8 %, however, means 22

% of the value of all chemicals produced in the German chemical industry. Considering such figures for the use of renewables one has to realize that there is a big margin between the production costs and the sale prices resulting in high profit. Therefore and also due to the environmental constraints there is a strong interest in Europe to broaden the base for such feedstocks. Some examples will be presented:

**1) The nature is the architect of the carbon framework for the desired compounds**

For example the selective conversion of mixtures of terpenes to the important intermediate p-cymene is of a high commercial interest. Such terpenes are widely and cheaply available as by-products from the orange and lemon juice production as well as from pulp and paper industry. The valuable p-cymene can be used, e.g. in the fragrance industry (non-nitrated musks), as a biodegradable solvent and as intermediate for the production p-cresol. The investigation of the catalytic behavior over various Pd-modified silica catalysts results in yields of up to 98 % depending on the mixture of the starting material. In addition to this topic a flavor for the production of fragrances and aroms based on renewables will be presented, too. Among them the synthesis of the sandalwood fragrances, the grapefruit arom and the mangofruit arom will be discussed.

**2) Oleoesters as feedstock for lubricants and biodiesel**

By far the largest amount of lubricants and pressure media used world wide is produced on the basis of mineral oil. In 1999, the consumption of lubricants in Germany was 1.159,900 t. 10 % of that amount was employed for loss lubrication (e.g. for chain saws or as release agents). In total, 520.000 t of lubricants are released into the environment.

Therefore the use of renewable feedstock is of high interest. The aim of our work presented is to improve the stability of rapeseed oil against oxidation and hydrolysis, by the addition of different carboxylic acids and alcohols to the double bonds in the presence of environmentally friendly heterogeneous catalysts resulting in high yields.

The 1st generation production of biodiesel FAME based on renewable feedstock such as palm oil, rapeseed oil, soya bean oil and brown grease is a hot topic of our days . We have been able to develop a bifunctional catalyst with acid sites and basic sites based on La doped zirconia. This kind of catalyst enables us to carry out the transesterification of the oleoesters with methanol simultaneously with the esterification of the free fatty acid (FAA). The raffination of the oleoesters or the preesterification of the FAA can be avoided by this new catalysts yielding in a more economical procedure. The catalyst development, its characterization and catalytic performance as well as the up scale in a continuous fixed bed reactor will be demonstrated.

The 2nd generation production of biodiesel will be illustrated on the conversion of oleic acid over Pd doped on amorphous silica alumina to achieve a mixture of hydrocarbons showing equal properties to conventional diesel

**3) Glycerin as platform molecule for value added chemicals**

In the biodiesel production of the 1st generation glycerol is produced as inevitable side product in 10%. In 2015 an amount of about 1 mio t/a glycerol is expected in Europe . As a result of that a lot of research is going on to convert that in high value added intermediates with a 3 C building block. The conversion of glycerol to acrolein and acrylic acid in high yields being competitive to the current technology based on propylene was developed in our group together with Arkema Comp. recently. That is a trend to get more independent from crude oil. This process is going to become commercialized.

In addition the possibility to convert glycerol to acrylonitrile will be discussed.

**4) Sugar and starch as platform feedstock for polymers etc.**

Metal-catalyzed oxidation of alcohols to carboxylic compounds is an important step for synthesis of fine chemicals. Particularly, the oxidation of the primary hydroxyl group in sugars and its derivatives such as starch and cellulose is important. The oxidized carbohydrates can be used as thickening, as gelling agents, in paints, as resins detergents co-builders, and as super absorbers (biodegradable diapers). Only a few reports describe procedures for the oxidation of primary hydroxyl groups which leave the secondary hydroxyl groups still intact. Such regioselective oxidation can be mediated by 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), but unfortunately thereby an environmentally hazardous hypochlorite/bromide system is used . Therefore our investigations focus on heterogeneously Ag-catalyzed procedure. For example, 99 mol % selectivity to methyl-a-

D-glucopyrasiduronic acid was obtained at 90 % conversion of the pyranoside over a silver-celite catalyst. Other examples are a new 2nd generation PLA process and production of isosorbite. Those examples will be discussed also in relation to chemical engineering aspects and its scale up procedures.

**PIETRO TUNDO**

*Professor of Organic Chemistry, Ca' Foscari University of Venice, Italy*

**The Chemistry of Dimethyl Carbonate**

In the use of CO<sub>2</sub> and CO<sub>2</sub>-based compounds as feedstocks, dialkyl carbonates (DACs) and in particular dimethyl carbonate (DMC) occupy a privileged position due to their low toxicity, high biodegradability and peculiar reactivity.

Nowadays, the large-scale production of DACs is carried out through clean processes (i.e., phosgene-free processes), which includes the direct insertion of CO<sub>2</sub> into epoxides, allowing – in principle – recycling of the carbon dioxide emitted during carbonate degradation. This prevents pollution at the source.

DACs are ambident electrophiles, which under appropriate conditions can undergo B<sub>Ac</sub>2- or B<sub>Al</sub>2-nucleophilic substitutions to give, respectively, alkoxycarbonylation and alkylation reactions. The reactivity of DMC is tunable: at 90 °C, methoxycarbonylations take place, whereas at higher reaction temperatures methylation reactions are observed with a variety of nucleophiles. In the particular case of substrates susceptible to multiple alkylations (e.g., CH<sub>2</sub>-active compounds and primary amines), DMC allows unprecedented selectivity toward mono-C- and mono-N-methylation reactions with a chemoselectivity up to 99%.

Moreover, DMC-mediated methylations are truly catalytic reactions that use safe solids (alkaline carbonates or zeolites), thereby avoiding the formation of undesirable inorganic salts as byproducts.

This groundbreaking achievement has definitely drawn attention toward the conception of procedures to activate the rather stable DACs with the aim of employing these compounds as green alternatives to their reactive chlorinated analogues.

This seminar reports also on DACs as alkoxycarbonylating agents and their applications in industry and fine synthesis, as well as alkylating agents including allylic alkylation using palladium catalysts and anchimerically driven alkylations via mustard carbonates analogues.

The reactivity of organic carbonates toward several substrates and under different reaction conditions is described along with some distinctive DAC-mediated cyclization and transposition reactions which can be carried out under continuous-flow conditions.

The many efforts devoted to improving the industrial suitability of organic carbonates have unveiled an intriguing and innovative chemistry as demonstrated by the numerous publications and patents published on these compounds over the last thirty years.

**GREEN MATERIALS**

**ALBERTO FIGOLI**

*Institute on Membrane Technology (ITM-CNR), Rende (CS), ITALY*

**Green Chemistry in Membrane Science and Technology**

Membrane-based operations are recognized as green emerging technologies. They are perfectly integrated in the sustainability context, due to the possibility to reduce energy consumption, enhance process efficiency, minimize/eliminate the use of chemicals, assure high-quality products and to have low maintenance and minimum operation requirements. Membrane technologies could play a crucial role for reaching sustainability objectives. In fact, in accordance with process intensification, i.e. «Producing much more and better with much less», they provide opportunities to improve or completely replace conventional, well established, large, expensive, energy intensive and polluting equipment or processes with alternatives that combine multiple operations into a more sustainable single apparatus or into fewer devices [1-2]. The majority of polymeric

membranes are produced *via* phase inversion technique. This procedure generally implies the use of organic, toxic solvents, needed to solubilize the selected fossil-based polymer. However, the more stringent environmental regulations for natural resources preservation and health safety, have considerably influenced the choice of chemicals in the last decade, encouraging the search of new, less toxic, greener alternatives. Recently, some emerging solvents have been proposed as valid alternatives for polymeric membrane preparation. Among them, several innovative non-toxic solvents offer promising perspectives for the green membrane preparation route [3]. The lecture will focus also on recent developments in membrane preparation via phase inversion by employing the greener solvents [4-5]. Moreover, the possibility of using of biopolymers derived from animal or vegetable sources and from bacterial fermentation products, fascinated the research along with the growing worldwide trend towards sustainability. The development of a suitable preparation procedure, allowing to tailor membrane structure and properties, will be presented. The potential applications of the fabricated membranes for water/vapour and gas separation will be also discussed.

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#### **KLAUS KÜMMERER**

*Director of the Institute of Sustainable and Environmental Chemistry (University of Lüneburg, Germany) and Scientific Director of Research and Education at the International Sustainable Chemistry Collaborative Centre (ISC3, Bonn, Germany)*

#### **Benign by Design-Designing Materials, Chemicals and Pharmaceuticals for Sustainability**

Chemistry both as science and technology is a success story that goes on since more than 150 years. It is the backbone of our high standard of living and health. There are more than 100 000 chemicals on the market, thereof 30 000 are estimated to be of relevance for the aquatic environment alone. An increasing number of chemicals, pharmaceuticals and materials also in terms of tonnage is expected for the future. In addition there are many more or less advanced materials in use such as plastics, composites, electronic materials and others. In other words the variety of chemicals and chemical products will also increase.

The backside of this success story is for example that resources for their synthesis and production are more and more under pressure. At the end of their life cycle more of these materials and molecules are dissipated in the environment polluting for example water resources as so called micro pollutants or being lost for further use or as resources of the future.

Chemistry is indispensable to meet the sustainable development goals of the United Nations. However, that will only be successful if chemistry contributes in a sustainable manner to sustainable development. A cornerstone thereof is the targeted design for sustainability of molecules and materials of the future. The concept Benign by Design addresses these issues. The concept itself and examples of it will be presented and discussed.

## REACTION MEDIA

### CHRISTOPHER BRETT

*Department of Chemistry, Faculty of Sciences and Technology, University of Coimbra, Portugal*

#### **Electrochemistry and green chemistry: from deep eutectic solvents to corrosion protection**

Deep eutectic solvents (DES) are a relatively new greener and lower-cost alternative to ionic liquids, or conventional organic solvents, and are used in a number of fields. The properties of DES will be reviewed, and compared with those of ionic liquids. Applications of DES will be indicated in polymer science as solvents or functional additives, in nanomaterials science and sensors and in metal processing (electrodeposition and electroless deposition) with a view to protection against corrosion.

### CINZIA CHIAPPE

*FRSC Department of Pharmacy, University of Pisa, Italy*

#### **Ionic liquid chemistry: twenty years of research to dispel myths and establish facts**

**Keywords:** Ionic liquids, biobased ionic liquids, biopolymers, added values biocompounds

Ionic liquids (ILs, organic salts that melt below 100 °C) have attracted considerable interest inside the broad scientific community in the last fifteen years; the combination of their unique physico-chemical properties, their tunability and the extremely high structural versatility (the evaluated number of possible ILs is more compatible with Astrophysics than with Chemistry!) have determined an incredible growth in the interest in these compounds for the more disparate technological applications. Interestingly, while ILs were growing in popularity, mythology flourished about both positive and negative attributes that each 'IL' is supposed to possess. Most of the papers on ILs, including recent reports, generally describe these liquid media as 'environmentally-benign solvents' in the first sentences, with the properties of non-volatility, thermal stability and non-flammability claimed in this regard. This despite it has been shown/proved that commonly used ILs have very low but not null vapour pressures (they can be distilled under appropriate conditions), that a large group of ILs is combustible and some commercially available ionic compounds are decidedly non-green. On the other hand, several ILs are truly thermally stable and some can be classified as non-toxic, indeed several are approved for food grade use. Thus, an excessive confidence or an unnecessary diffidence can lead to inappropriate and even dangerous uses of ILs, as well as to a lack of use, although appropriate. These opposite behaviours arise essentially from the unjustified attribution of features which have been observed for selected classes of ILs, to all ionic liquids. Actually, due to the generic nature of the definition of ILs as low-melting salts, the properties of ILs vary extensively and probably the most attractive feature of ILs is just the fact that the extremely high variability of ions can give rise to salts with uncommon properties and behaviours. Here, some common myths and established facts will be critically revised in light of our experience in the field, of course taking into account also the vast literature on the different topics.

Ionic liquids are undeniably interesting compounds with a wide range of potential applications and with a unique ability to be designed to meet a specific set of requirements. These features cannot be stifled by false myths and distorted truths.

### NICHOLAS GATHERGOOD

*ERA Chair of Green Chemistry, Division of Chemistry, Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology*

#### **The Design Of Safer Chemicals: Are Mineralisable Compounds An Achievable Goal?**

**Keywords:** Green toxicology, biodegradation, mineralization, ionic liquids, catalysis, green chemistry metrics  
The format for this summer school seminar is an interactive journey where the student stops at stations representing most of the 12 Principles of Green Chemistry. At the final stop we can answer the title question, The Design Of Safer Chemicals: Are Mineralisable Compounds An Achievable Goal?

The journey undertaken encompasses three fields of green chemistry research; ionic liquids (ILs), eco(toxicity) assessment and catalysis. In particular, one such study we have undertaken is directed towards ILs which can also catalyse reactions. This overlap between organocatalysis and IL research enables us to design low toxicity and potentially biodegradable catalysts based on the biological screening data of ionic liquids.[1,2]

Assessment of the performance of a new catalyst, in tandem with the (eco)toxicity screening and biodegradation testing allows the chemist to develop greener synthetic methods.[3-5] We have designed a library of aprotic ILs which can act as Brønsted acid catalysts with low antibacterial and antifungal activity.[1,4-5] Toxicity evaluation of all the ILs prepared was performed to establish the influence of ester or amide groups in the cation. Antifungal and antibacterial toxicity results show that the ILs did not inhibit the growth of any organism screened at concentrations of 2.0 mM. Biodegradation of the novel ILs was also investigated in “CO<sub>2</sub> Headspace” test (ISO 14593).

Our work which includes green chemistry metrics feedback, investigates the effect of substitution on the imidazolium ring on biodegradation, toxicity and activity of the catalyst in acetalisation reactions.[4,5] This enables our team to recommend the ‘greenest’ imidazolium compound of our series for further applications. Lessons learned in the development of these catalysts has been applied to the design of safer IL solvents and recently surfactants. In particular, selection of compounds to be included in a test study is governed by the predicted high propensity to biodegrade (even mineralise) in the environment.[6,7]

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NG acknowledges this work is supported by EU 7th Framework Programme for Research, Technological Development and Demonstration Activities, under grant agreement activities No. 621364 and Estonian Research Council grant PUT 1656.

## ALEXEY ZANIN

*UNESCO Chair in Green Chemistry for Sustainable Development Dmitry Mendeleev University of Chemical Technology of Russia*

### **Ionic Liquids – Green Solvents or Not?**

Ionic liquids have been long considered as green solvents that possess high thermal and chemical stability (even under rather drastic conditions) and catalytic activity. Ionic liquids were used in our investigations as a reaction medium component in polymerization processes. This helped to reach higher conversion, polymerization rate etc. in phosphorus and sulfur conversion to polymeric forms.

It should be noticed, that ionic liquid can be used not only as an individual solvent but also as an additive to nonpolar solvents (hexane, toluene, diethyl ether, tetrachloromethane), so the reaction medium could be heated with microwave radiation. This allows to study processes with ionic liquids under microwave radiation as well as under high-energy radiation.

Some of results of this experiments lead to hypothesis that ionic liquids are not so green and stable, so the limits of use the ionic liquids as green solvents should be precised.

## ANALYTICAL CHEMISTRY & GREEN CHEMISTRY FOR RESTORATION

### JAN LABUDA

*Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Slovakia*

#### **Approaches of Analytical Chemistry Reflecting Principles of Sustainable Chemistry**

**Keywords:** green analytical chemistry, sustainable methods development, sample preparation, experiments arrangement, materials and chemicals characterization

### ROCCO MAZZEO

*Full professor of Chemistry for Cultural Heritage and Head the Microchemistry and Microscopy Art Diagnostic Laboratory of the University of Bologna, Italy*

#### **Materials and methods for the conservation of works of art. From current practice towards a green attitude in art conservation: new bio-based organogels for the cleaning of bronzes and paintings.**

In the last decade, solvent-gels used for the removal of aged varnishes or coatings from artwork surfaces have gained considerable popularity. The main reason is the ability to retain solvents and provide a controlled and efficient superficial cleaning action<sup>[1,2]</sup>. To date, traditional cleaning methods, based on the application of liquid solvents, present serious drawbacks mainly due to the difficulty of controlled applications and their harmfulness to humans, environment and artworks.

Recently, we have proposed new green gels for the cleaning of paintings. The gels have been based on poly-3-hydroxybutyrate (PHB) as gelling agent and  $\gamma$ -valerolactone (GVL), as solvent for the removal of different terpenic and synthetic varnishes from oil and water sensitive egg tempera painting<sup>[3,4]</sup>.

Moreover, an advanced system for the cleaning of wax-based coatings applied on indoor bronzes has been also proposed. To this aim we developed a new kind of eco-friendly and easily peeled gel based on PHB, biodiesel (BD) and Dimethyl carbonate (DMC). BD is a mixture of methyl esters obtained from palm oil, which acts as cleaning agent while DMC as cross-linking agent, which partially solubilises PHB.

After the preliminary characterization of chemical and physical properties of the gel, an ad hoc analytical protocol was implemented to evaluate both the cleaning efficiency and the release of residues on the treated surfaces. Standard samples were prepared following ancient recipes and submitted to spectroscopic and chromatographic analysis before and after the cleaning procedures.

Finally, the performances of PHB-BD/DMC gel were assessed on a real case of study presenting a wax-based coating: the Pulpito della passione attributed to Donatello, which dates back to 1460 A.C. In situ analysis demonstrated the high cleaning efficiency of the proposed systems also for the removal of aged coatings.

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### COSTANZA MILIANI

*CNR-ISTM (National Council of Research Institute of Molecular Science and Technologies), Perugia, Italy*

#### **Non invasive spectroanalytical methods for a sustainable diagnostic in heritage science**

In situ non-invasive methods have experienced a significant development in the last decade because they meet specific needs of analytical chemistry in the field of cultural heritage where the analytes are a wide range of inorganic, organic and organometallic substances in heterogeneous matrices belonging to precious and often

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unmovable objects. The lecture will give an overview on spectroanalytical methods tailored for heritage science applications underlining their role in the long-term sustainability of our cultural heritage.

### **EGID B. MUBOFU**

*Vice Chancellor, University of Dodoma (UDOM), Tanzania*

#### **Standardization for sustainable development**

Standardization and sustainable development are inseparable entities for global sustainable development and in attaining sustainable development goals (SDGs). Whereas Standardization is concerned with the development and provision of standards and the supply of information on standards to interested parties, sustainable development insists on the development that meets the needs of the present without compromising the ability of the future generations to meet their own needs. The latter can only be possible if there is consistent application of standards in processes and services which would finally result into sustainable business and economic growth of the society. Normally this is possible through quality infrastructure in any country that guarantees conformity to standards and compliance to relevant legislation and regulations. The pillars of Quality Infrastructure (QI), encompasses elements of standardization, metrology (legal, scientific and industrial), accreditation and conformity assessment as building blocks. The QI is a cornerstone to regional and international trade because countries' economies cannot grow and survive in the absence of trade of good quality products and services to attain sustainable development. The national quality infrastructure (NQI) support sustainable development by providing relevant technical support on safety and quality of all products and services offered and hence leading to product international recognition. The primary premise of modern industrialization with quality industrial production and safety guarantee lie in the hands of conformity to standards which cannot be achieved in the absence of a well-established quality infrastructure. This presentation will introduce standardization and briefly spell out its role in attaining sustainable development of the society.

### **ANTONIO SANSONETTI**

*Institute for Conservation and valorization of Cultural Heritage National Research Council - Milan*

#### **Green chemistry at the service of Conservation: cleaning artworks with gels**

Cleaning art surfaces is very often a challenging operation: effectiveness, selectivity, controllability and a gradual action are among the requirements searched by best practices. Moreover the safety of the morphological and compositional features of the art object is of crucial importance. Chemistry acts in supporting conservators choices with traditional and innovative systems: organic solvents, chelants, surfactants could be classified in the first group; gels and micro-emulsions in the second. The special case of polysaccharide substances used in gel formation, such as agar, will be introduced in the speech. Chemical composition and physical features will be highlighted, taking into account the possible applications on delicate surfaces; addition of some chemicals enhancing the cleaning action will be presented. The benefit-disadvantage ratio will be discussed in the framework of green chemistry issues, with the aid of several recent applications on real art objects.

TEACHERS' POSTER ABSTRACTS

RENEWABLES & GREEN ENERGY

**Title:**

**Catalysts derived from sustainable natural and value added alkaloids from poppies**

**Authors & affiliations:**

*E. Silm<sup>1</sup>, P. Pata<sup>1</sup>, J. C. Kruis<sup>1</sup>, A. Sikerina<sup>1</sup>, I. Pata<sup>2</sup>, T. Kanger<sup>1</sup>, N. Gathergood<sup>1</sup>* *Tallinn University of Technology, Estonia,*  
*<sup>2</sup>IVEX Lab, Estonia*  
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**Abstract:**

Alkaloids are a group of naturally occurring compounds that contain nitrogen heterocycles. Morphine and similar alkaloids are classified based on the 'morphinan' skeleton. The morphine alkaloids are well studied in medicinal chemistry [1] but their use in asymmetric organocatalysis is a new research area. The rigid and well-defined morphine scaffold can be used as a source of chiral induction in asymmetric catalysis. A major advantage of morphine is that it is abundant, renewable and cheap raw material.

In this work, morphine alkaloids can be modified into quaternary ammonium salts, secondary amines, and chiral phosphoric acids which then can be used as phase transfer catalysts (PTC), aminocatalysts or Brønsted acid catalysts correspondingly. The initial studies show that only the quaternary ammonium salts of codeine show enantioselectivity.

Opioid salts were tested in functional luciferase assay of opioid receptor signaling. Our data show that these are less potent activators of OR signaling than morphine.

The authors acknowledge funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement #621364 (TUTIC-Green).

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Keywords: Alkaloids, organocatalysis and opioid receptor signaling

## REACTION MEDIA

**Title:**

**Biodegradation studies of a series of dipeptide based ionic liquids and their transformation products**

**Authors & affiliations:**

*G. Raba<sup>1</sup>, I. Kapitanov<sup>1</sup>, Y. Karpichev<sup>1</sup>, V. Gupta<sup>1</sup>, S. Sudheer<sup>1</sup>, K. Kümmerer<sup>2</sup>, R. Vilu<sup>1</sup>, N. Gathergood<sup>1</sup>*  
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**Abstract:**

Ionic liquids (ILs) with their potential for high recyclability, low volatility, low flammability and potential for synthesis from renewal materials are often seen as „greener“ alternatives to organic solvents. However, early generations of ILs were designed to be robust and inert to a range of chemical conditions and thereby have been shown to be poorly biodegradable.[1-2] As ILs are increasingly being used in large-scale industrial processes [3], the need to assess their biodegradability is important to avoid possible release of yet another source of persistent organic pollutants to the environment. Our group in collaboration with Prof. Ü recently published a mineralizable pyridinium IL alleviating the problem of persistent breakdown products.[4]

Several standard tests are in place for evaluation of biodegradability with closed bottle test (OECD 301D) being one of them. Modification of this test [5] allows for a high-throughput screening of compounds for their biodegradability. In this poster results obtained using modified closed bottle test on a series of dipeptide based ionic liquids and their proposed transformation products are presented.

Authors acknowledge funding from European Union's Seventh Framework Programme for Research, Technological Development, and Demonstration under Grant Agreement no. 621364 (TUTIC-Green) and Estonian Research Council Grant PUT1656.

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Keywords: Biodegradation, transformation products, mineralisation.

STUDENTS' POSTER ABSTRACTS

ABSTRACT INDEX (Alphabetical Order)

Asmaa Ajarroud

**Study and the acid character of Molybdenum Oxide Supported on The zinc Orthophosphate catalysts: Use of isopropanol decomposition as test reaction**

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Egle Rosson

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## RENEWABLES & GREEN ENERGY

### Green synthesis of luminescent carbon quantum dots from coffee

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**Keywords:** GO, FTIR, optical absorption, photoluminescence

The hydrothermal technique at low temperature was used to elaborate our nanoparticles (NPs) of graphene oxide (GO) from a natural Carbon source (coffee). FTIR confirm the different vibratory bonds of the elaborated GO. The optical absorption spectra show an absorption band located approximately at 270 nm which shift toward red for high concentration of GO dispersions. Photoluminescence spectra, shows a bathochromic emission, more intense for an excitation of 310 nm, and especially for low concentrations, gives a rise to an emission band situated at 407 nm. The results of the multi-exponential time decay gives a lifetime of:  $\tau = 4,07 \pm 0,03$  ns. The fluorescence of our Carbon NPs, shows their possible applications in the medical field.

**Fractionation of willow bark for combined production of extracts and fiber bundles**

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**Keywords:** Sclerenchyma fiber bundle, Willow bark, Extractive

Although willow bark is best known as a rich source of polyphenolic compounds, it is also a potential feedstock for biorefinery processes in general. The morphology and chemical composition of inner bark of willow hybrids were analyzed as the first step towards complete willow biomass valorization. The most characteristic features of willow inner bark are the high contents of ash and extractives and the presence of bundles of relatively long and thick-walled fibers.<sup>1</sup> Recently we discovered that picein, triandrin and catechin were extracted in ca. 14 % overall yield from willow bark by hot water (20 min at 80 °C).<sup>2</sup> NMR spectroscopy and wet chemical analyses demonstrated the guaiacyl (G) was the predominant unit in the willow bark lignin over syringyl (S) and *p*-hydroxyphenyl (H) units.<sup>3</sup> The aforementioned knowledge on lignin structure in willow bark is the key for developing appropriate methods for the separation of its unique fiber bundles for specific applications, such as composites,<sup>4</sup> to fulfill the whole willow biorefinery scheme<sup>1</sup>.

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**The Working Pair "LiCl/Multi-Wall Carbon Nano-Tubes/Pva" - Water For Thermal Energy**

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**Keywords:** Sorption thermal energy storage, composite "salt/matrix", water sorption dynamics

Sorption heat storage (SHS) is a promising technology towards efficient use of renewable energy sources. Enhancement of the thermal energy storage capacity (TSC) of the adsorbents and the specific power (SP) of the unit is the key issue to be solved for further dissemination of this technology. Recently, the composite "LiCl inside Multi-Wall Carbon NanoTubes" (LiCl/MWCNT) with high TSC under conditions of daily SHS cycle, has been suggested [1]. Owing to large pore volume and particular S-shaped water adsorption isotherms, this composite demonstrate large TSC equal to 1.7 kJ/g under conditions of heat storage cycle driven by low-temperature (75-85°C) heat source. Along with high TSC of the adsorbent, the SP achievable in the storage unit during the heat storage and release stages is of primary importance for SHS, particularly, for short term daily storage cycles. This work addresses: 1) shaping the new composite available as a powder as grains using polyvinyl alcohol as a binder; 2) the study of water sorption equilibrium and TSC of the LiCl/MWCNT/PVA composite; 3) investigation of water sorption dynamics under conditions of the daily SHS cycle on small, but representative fragments of real finned flat-tube heat exchanger; 4) evaluation of the SP of the heat storage/release stage. The characteristic curves of water sorption on the LiCl/MWCNT/PVA composite are step-wise. The steps on the curves are attributed to the formation of two hydrates LiCl·H<sub>2</sub>O and LiCl·2H<sub>2</sub>O. The TSC of the LiCl/MWCNT/PVA reaches 1.5-1.6 kJ/g. It was shown that the dynamic curves of water sorption obey the exponential behavior with the characteristic time  $\tau = 100-300$  s. The specific power of the heat release at conversion 0.8 varies in the range of 4.2-4.3 W/g. That for heat storage equals 9.7-9.8 W/g. High values of the SP along with the large TSC of the new composite demonstrate it's promising potential for SHS.

**Acknowledgment**

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## Synthetic Routes Towards Triazole Cannabidiol Analogues

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**Keywords:** Cannabidiol, Cancer, Triazole

Preparations from the Cannabis plant have been used for many centuries, both medicinally and recreationally. Cannabinoids are the main active constituents found in the Cannabis plant; and over 90 cannabinoids have been discovered. Although the specific biological activity of some cannabinoids have not yet been determined, it has been shown that this unique set of compounds certainly holds tremendous medicinal value.<sup>1</sup> The structure of the main psychoactive compound, tetrahydrocannabinol (THC, Figure 1), was elucidated in the early 1960s, and this led to the hunt for possible binding sites within the human body.<sup>2</sup> The cannabinoid receptors (CB1 and CB2) are part of the endocannabinoid system; and this system, along with its ‘Cannabis-like’ substances, control many functions in our brain and immune system. The discovery of the endocannabinoid system opened up a new and exciting field in medicinal research. This research has shown that certain cannabinoids, including THC, possesses anti- proliferative and pro-apoptotic effects; and have the ability to interfere with cancer cell migration and metastasis. However, the clinical use of THC is limited by its unwanted psychoactive side-effects. As a result, interest in non-psychoactive cannabinoids, in particular cannabidiol (CBD, Figure 2), has increased significantly.<sup>3</sup> CBD offers the hope of a nontoxic therapy that could achieve significant results without any of the negative side effects associated with standard cancer therapy. The aim of this project was therefore to synthesize CBD analogues in order to observe the differences in efficiency of these compounds on cancer cells. An interesting aspect of the analogues in this study, is that the scaffold contains a 1,2,3-triazole ring (Figure 3) instead of the usual benzene ring present in the CBD structure.

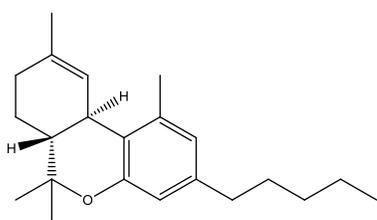


Figure 1 Structure of THC

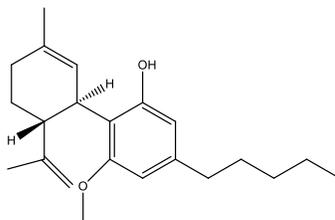


Figure 2 Structure of CBD

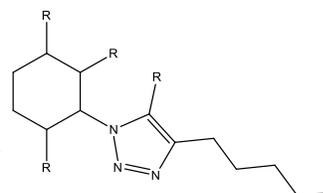


Figure 3 General structure of CBD analogues

This change is possible as a similar spatial distribution can be achieved with the triazole ring.<sup>4</sup> Initially, a model system was used to determine the ideal copper source for the 1,4-triazole ring formation for this specific system.<sup>5,6</sup> The conditions of the ruthenium mediated click reaction was also investigated on the model system, as this gave the opportunity to incorporate a hydroxyl-functionality onto the triazole ring.<sup>7</sup> Subsequently, a slightly more complex system was developed which involved a Michael addition onto the structure of 2-cyclohexen-1-one, affording the azide counterpart needed for the click reactions. Finally, a third scaffold was developed where the main enantiomer of menthol was used as a building block to produce different diastereomers of these interesting CBD analogues.<sup>8</sup>

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**Synthesis Of New Eco-Friendly Copolyesters From Fully Renewable Resources: Poly( $\epsilon$ -Caprolactone-Co-Pentylene 2,5-Furandicarboxylate)**

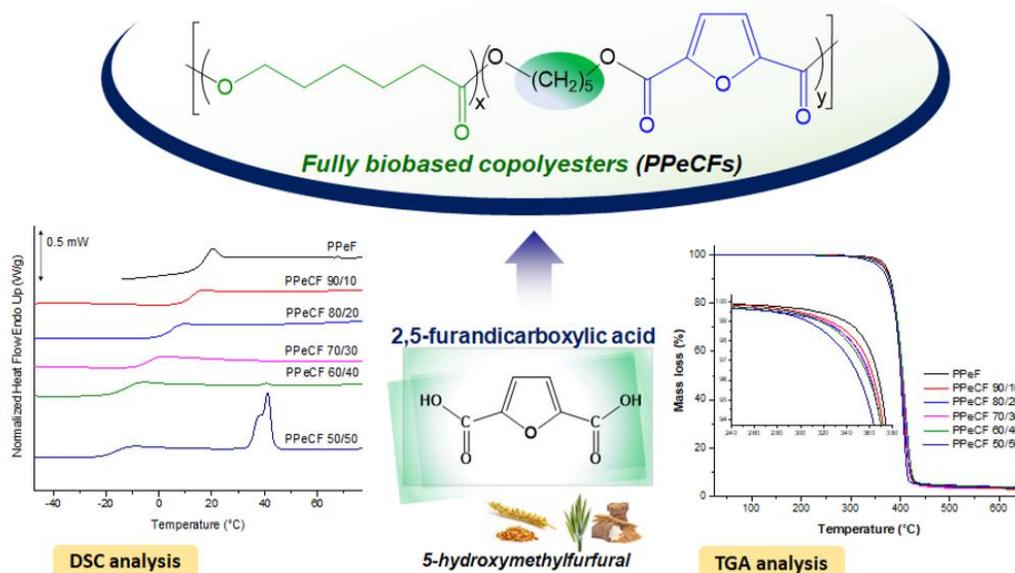
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**Keywords:** 2,5-furandicarboxylic acid, fully biobased copolyesters,  $\epsilon$ -caprolactone, sustainable polyesters.

A new fully bio-based copolyesters series, poly( $\epsilon$ -caprolactone-co-pentylene 2,5-furandicarboxylate) (PPeCFs), have been synthesized from dimethyl-2,5-dicarboxylate,  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and 1,5-pentanediol covering the compositions range of 10, 20, 30, 40 and 50 %  $\epsilon$ -caprolactone content. The obtained copolymers, through a two-step melt polycondensation procedure and using stannous octoate as catalyst, were duly characterized in terms of chemical structure by <sup>1</sup>H NMR to determinate their compositions and sequence distribution and on the other hand in terms of thermal properties by using Differential Scanning Calorimeter (DSC), wide-angle X-ray diffraction (WAXD) and thermogravimetric analysis (TGA). DSC results showed an amorphous behavior of PPeCFs, while their glass transition temperatures (T<sub>g</sub>) ranging from -16.1 to 16.9 °C steadily increased with the decrease of molar content of  $\epsilon$ -CL in the prepared copolymer composition. The intrinsic viscosity values [ $\eta$ ] (IV) increased from 0.34 to 0.42 dL/g with increasing  $\epsilon$ -CL comonomer content respectively from 10 to 50 %. Thermogravimetric analysis (TGA) reveals an excellent thermal stability up to temperatures exceeding 365 °C for all prepared copolyesters. This study allowed to confirm that the homopolyester PPeF insertion into the prepared polymer backbone is distinctly effective in enhancing of T<sub>g</sub> of synthesized materials.



**Figure 1** – Synthesis and characterization of (PPeCFs) copolymers.

**Catalytic valorization of glycerol mediated by transition metal Graphitic Carbon Nitride composites**

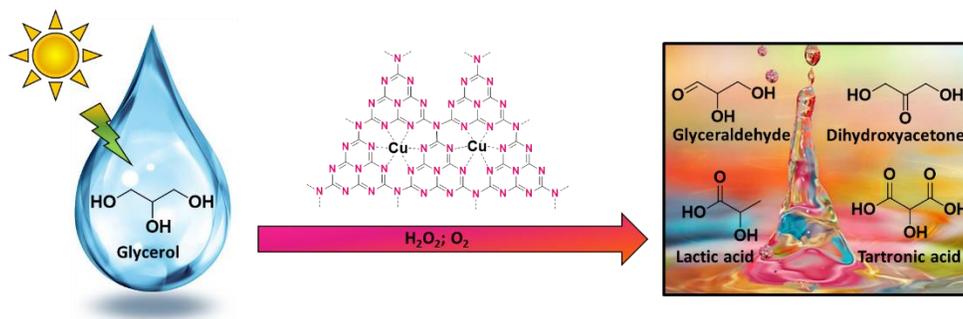
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**Keywords:** graphitic carbon nitride, photocatalysis, glycerol, oxidation.

The development of environmentally sustainable industrial chemical processes has become increasingly important in recent years. It is vital that such processes incorporate ‘green’ chemistry in the catalytic transformations. It is therefore necessary to develop metal based catalysts which are non-toxic, inexpensive, recyclable and synthesized from renewable precursors. These catalysts also need to exhibit excellent activity and selectivity in catalytic processes which transform waste and biomass into value added products. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a conjugated polymer consisting of tri-s-triazine (heptazine) units which can be synthesized from inexpensive nitrogen rich precursors. This material serves as an organic semiconductor and has been found to exhibit excellent catalytic properties, especially in the field of photocatalysis.<sup>1</sup> It is also a very stable, low cost material which can be used as an organic support for various molecules and elements.<sup>2</sup> These catalysts can therefore be recycled and reused for a specific transformation.<sup>3</sup>



*Scheme 1: Photocatalytic oxidation of glycerol to value-added products in aqueous media, using Cu/g-C<sub>3</sub>N<sub>4</sub> as*

In light of the above, catalytic composite materials based on graphitic carbon nitride as a matrix, have been synthesized. More specifically, first row transition metal graphitic carbon nitride composites have been prepared using different synthesis methods to incorporate the metal into the framework. These synthesis methods include the synthesis of g-C<sub>3</sub>N<sub>4</sub> metal composites via intercalation of first row transition metal ions within the native g-C<sub>3</sub>N<sub>4</sub> framework and the thermal polymerization of dicyandiamide in the presence of first row transition metal ions. A variety of solid state characterization techniques have been employed to characterize the composite materials. Characterization techniques include: FT-IR, powder XRD, elemental analysis, UV-vis diffuse reflectance spectroscopy, TGA, SEM and ICP-OES. These transition metal g-C<sub>3</sub>N<sub>4</sub> composites were applied in the oxidation of a bio-renewable resource, specifically glycerol (Scheme 1), in both the presence and absence of light. The reaction was conducted at different temperatures and pressures, using mild oxidants such as hydrogen peroxide and molecular oxygen. The results of this investigation are reported here.

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**Biobased Chemistry and Technology: Synthesis of Galactaric Acid Lactone and its Reactivity Towards N, O, S Bases**

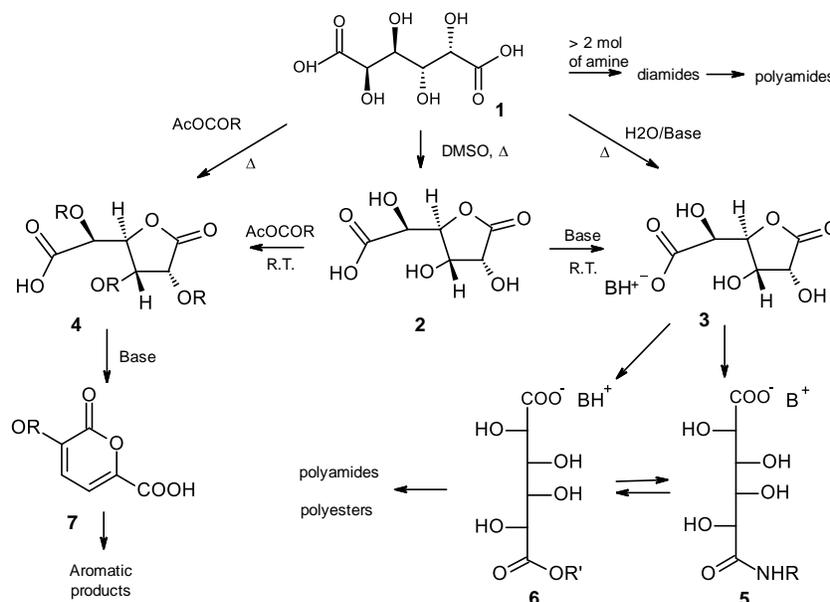
J. Li<sup>1</sup>, G. Leonardi<sup>1</sup>, R. Sebastiano<sup>1</sup>, A. Truscello<sup>1</sup>, C. Gambarotti<sup>1</sup>, A. Citterio<sup>1</sup>

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**Keywords:** galactaric acid lactone, galactarate lactone salts, galactaramide salts, aldaric polyamides-polyesters.

Galactaric acid (**1**) [one of the more representative aldaric acid, the general class of  $\alpha,\omega$ -dicarboxylic acids of C-6 and C-5 sugars] is a platform chemicals available in nature and easily recovered by processing selected biomass (i.e. orange and apple peels) or by fermentation of primary metabolites. As other aldaric acids, this compounds can be a valuable source of bioderived chemicals, polymers and materials [1]. The present study is focused on the lactone of galactaric acid (**2**), a scarcely investigated derivative with relevant potentialities, as suggested by our explored chemistry of Scheme 1. [2]



Scheme 1. Summary of chemical conversions of galactaric acid lactone investigated in this study.

Recent data obtained for these systems will be discussed, i.e.: a) efficient synthesis of **2**; b) its conversion by different inorganic and organic bases to the corresponding salts **3**; c) their conversion under mild conditions to primary amides **5** and esters **6** and to their homo and co-polymers; d) esterification of **2** to **4**; e) dehydration of **4** by a base to pyrones **7** and further converted into aromatics.

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D. A. Thomas, T. Virtanen & M. G. Wiebe, *Separation Science and Technology* **2017**, 1, ISSN: 0149-6395

**JULY 7-13, 2018 – VENICE**

**Production of activated carbon from sugarcane bagasse: Optimization using response surface methodology**

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**Keywords:** Bagasse; Activated carbon; Response surface methodology

Activated carbon is the most widely used adsorbent for dye removal because it has a high adsorption capacity and a large surface area for organic compounds. However, the use of activated carbon is typically limited due to its high cost. Therefore, in recent years, the use of activated carbon (AC) from lignocellulosic wastes has gained a lot of research interest because of its great economic and environmental value.

The goal of this study was to find the optimum production conditions for making an AC from sugarcane bagasse via chemical activation with phosphoric acid ( $H_3PO_4$ ) and heat treatment. The relationships among the activation parameters were investigated by using the central composite design under response surface methodology (RSM). Seventeen combinations of the three variables namely; impregnation ratio (1, 1.5, and 2); activation time (30, 60, and 90 min); and activation temperature (400, 500, and 600 °C) were optimized based on the responses evaluated (yield and adsorption capacity).

In conclusion, RSM has proven to be a good tool in optimization analysis to get not only optimum production conditions points but ranges, which are crucial for the flexibility of the production process, as well.

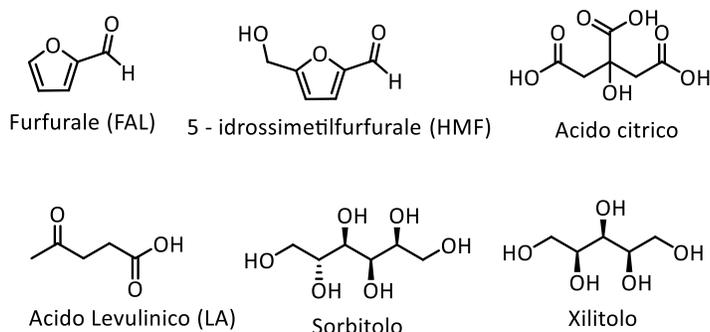
Synthesis and Functionalisation of Bio-based Platform Chemicals from Renewables Resources

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In the last years, development and study of the biorefinery have attracted the interest of both academia and industry. In fact, biorefinery involves those processes based on the exploitation of the biomass and thus alternative to the refinery.<sup>1</sup> The 'biomass' incorporates a variety of chemicals, such as protein, fatty acids, lipids and carbohydrates, which may represent a very attractive and cost-efficient renewable resources of carbon. Among these products, carbohydrates represent about 75% of biomass and thus, through their functionalisation, they play a pivotal role



not only as energy source, but also as suppliers of bio based platform chemicals. 5-hydroxymethylfurfural, furfural, levulinic acid, sorbitol, citric acid and xylitol (Figure 1) are solely few examples bio based platform chemicals obtained from carbohydrates and which can be used as green solvents, fuel additives, monomers for biopolymers, etc.<sup>2</sup> Herein, we report synthesis and functionalisation via the dialkylcarbonates chemistry of two specific bio-based platform chemicals: Isosorbide and HMF.<sup>3</sup> The developed and optimised synthetic procedures involved mild reaction

**Figure 1.** Example of bio-based platform chemicals

achieve in quantitative yield. Isosorbide and HMF derivatives synthesised can be used as green solvents monomers for bioplastics and fuel additives.

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**JULY 7-13, 2018 – VENICE**

**Corrosion Inhibiting Formulations from Residues of the Cashew Industry**

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**Keywords:** Eco-friendly, corrosion, residues

Global demand for chemicals from renewable sources has grown in recent years and a variety of raw materials from renewable sources is currently being tested in oilfield applications. Their co-products and residues can add value to biomass production chains, mainly to inputs and final products of sectors of the economy such as foods and fuels. In the petroleum industry, in particular, corrosion is a problem that leads to significant costs for operations that extend from exploratory drilling to storage of fuels and petrochemicals. Pipelines, especially in deep and ultradeep offshore fields, are susceptible to corrosion, requiring mitigation methods, the most efficient being the use of inhibitors.

Green inhibitors have received considerable attention since they have a lower impact on the environment and result in much lower degree of health problems. A potential source of these inhibitors is cashew nut shell liquid (CNSL), a by-product of the cashew industry, which contains alkylphenols with an unsaturated side chain. The high electron density allows adsorption of these compounds to the metal surface. The objective of this work was the development of inhibiting formulations from CNSL distillation residues to protect carbon steel API P-110 in 15% HCl. The residue was combined with two solvents, an ether and a short chain alcohol, to prepare two formulations, F1 (containing the residue as active substance) and F2 (containing the residue and another alcohol). The performance of the formulations was evaluated in gravimetric measurements at 40°C, 60°C and 80°C (2% v / v), and electrochemical measurements at 60°C (0.5-6% v / v). The residue was characterized by FTIR, <sup>1</sup>H-NMR and TGA, indicating an aromatic polycondensate structure of high molecular mass. The gravimetric measurements revealed that at 40°C and 60°C, F1 and F2 originated in corrosion rates within the industrial criterion, while at 80°C only F2 reaches 99.5% efficiency. The electrochemical measurements are in agreement with the gravimetric results, supporting the proposed mechanism of inhibition. The properties of the inhibiting film were confirmed by MEV-EDS and FTIR. It appears that F1 is adsorbed physically, and F2 is adsorbed physically and chemically to the metal surface.

There are indications that the formulations have an innovative potential and can be applied in acidizing fluids, with F1 being appropriate for wells with temperatures up to 60°C, and F2 for those up to 80°C. These formulations add value to a by-product of the cashew industry and have a lower environmental impact than several of the commercial formulations presently in use.

**Solvent-free synthesis of  $\gamma$ -valerolactone from biomass-derived levulinic acid by arene Ru<sup>II</sup> and Ir<sup>III</sup> pre-catalysts**

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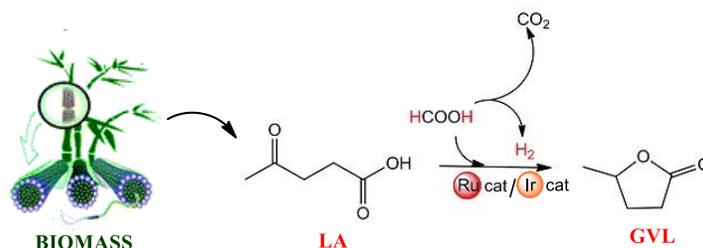
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**Keywords:**  $\gamma$ -Valerolactone, Solvent-free, Recyclable catalysts

The sources of carbon for the production of fuels and chemicals have for the past century been derived from fossil resources (coal, crude oil and natural gas). However, burning of these fossil products causes environmental pollution and also has a great impact on the climate. To avoid these problems, which are of great concern to the world at large, scientists are looking towards the utilization of alternative sources of carbon for the production of these fuels and chemicals. Plant biomass is one of such important alternative sources of carbon. Carbohydrate polymers in plant biomass can be transformed into many chemicals including ethanol, n-butanol, sorbitol, furfural, 2,5-hydroxymethylfurfural and levulinic acid (LA). In turn, levulinic acid can be converted into  $\gamma$ -valerolactone (GVL), which is one of the most promising renewable platform molecules. GVL can be transformed into various chemicals including, 1,4-pentanediol, 2-methyl tetrahydrofuran and 2-butene, and also serves as an intermediate in the production of various biofuels as well as commodity and fine chemicals. Herein, we report selective and efficient solvent-free hydrogenation of levulinic acid (LA) into  $\gamma$ -valerolactone (GVL) (Scheme 1) by new pyridinyl-imine ruthenium(II) and iridium(III) complexes as catalyst precursors.

**Scheme 1:** Synthesis of bio-derived  $\gamma$ -valerolactone



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**JULY 7-13, 2018 – VENICE**

**Biomass Waste To Energy: Investigating Syngas Production From Pyro-Gasification Of Sawdust Blends Of Invasive Trees And Tropical Tree Species**

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**Keywords:** Pyro-gasification; Biomass; Invasive Alien Plants

Epileptic power generation and access to electricity in remote areas remains a major barrier to economic development in Sub-Saharan Africa (SSA). A genuine off-grid power generation from renewable sources such as wood can eliminate bottlenecks caused by centralized power generation and long-distance transmission and distribution networks lacking substantial coverage in remote areas within the region. The SSA occupies 16% of the global forest estate which supports its very lucrative sawmill industry making it the largest supplier of sawn wood products consumed globally. With the ever-rising demand for sawn wood, Africa's sawmill industry production levels are expected to double with a resultant increase in sawmill waste generation. Sawdust is classified as an unavoidable waste across the wood industry supply-chain and is generated in huge commercial rates. Nigeria faces an impending environmental catastrophe caused by poorly managed sawdust waste generated across the country at an estimated 5.2 million tons/year. Moreover, in order to salvage the region from drought, South Africa implements the eradication of fast-growing and highly invasive alien trees occupying over 10 million hectares and consuming an estimated 3 billion m<sup>3</sup> of water annually, thereby generating huge amounts of biomass. Utilizing such wastes for off-grid power generation is vital. Pyro-gasification is a hybrid of pyrolysis and gasification for increased efficiency in the thermochemical conversion of wood to syngas. By blending sawdust obtained from tropical trees common in sawmills with those from invasive trees in different ratios as feedstock for pyro-gasification, syngas quality can be optimized for power generation. Firstly, the lignocellulosic composition of six invasive tree samples and four tropical hardwoods was evaluated in relation to parameters such as proximate and ultimate characteristics, density, surface morphology and thermogravimetry. Results of the samples were analyzed and compared to determine their suitability as feedstock for the pyro-gasification process. Secondly, the most ideal biomass will be selected and mixed in varying ratios for a laboratory-scale pyro-gasification process for syngas production.

**JULY 7-13, 2018 – VENICE**

**Expedient synthesis of 6-deoxy-6-amino chitosan**

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**Keywords:** Chitin, chitosan, 6-deoxy-6-amino chitosan

Chitosan attracted significant scientific interest with a broad spectrum of applications during the last two decades. It found an enormous popularity due to its biocompatibility and chemical versatility. Many early reviews have been written on the general applications, while recent reviews has become more focused on specific applications such as drug delivery, tissue engineering, wound healing, water purification, cosmetics, textiles, heterogeneous catalysis and many more. Monographs on the biological safety profile of chitosan classified it as a generally regarded as safe (GRAS) material. Its unique physical properties due to the amino group, its biodegradability and renewable nature, favour chitosan as a polymer that will gain rapid acceptance in the market place. Chitosan has been reported as a promising material for gene and drug delivery as well as for tissue engineering and regenerative medicine.<sup>1</sup>

The poor solubility profile of chitin restricted its utility in comparison with the sparingly soluble chitosan. However, C-2 and C-6 modified chitosans have demonstrated greatly improved solubility depending on the hydrophobicity or hydrophilicity of the new polymer. Modified chitosan by virtue of converting the 6-hydroxy group in the polymer to a 6-amino-group found utility in gene delivery. The advantage that the modification holds is that a sparingly soluble polymer now becomes completely soluble in aqueous media. Solubility in aqueous media broadens the scope of applications of the polymer.<sup>2</sup> 6-Deoxy-6-amino chitosan is the simplest derivative of chitosan to contain an amine at C-6. The reported uses of this polymer includes gene transfection, antioxidant ability, in cell growth, as a catalyst support and in argentation chromatography. This polymer has been previously synthesised via a halogenated and later a tosylated intermediate. The current study aimed to improve the synthesis of this valuable polymer with an emphasis on a greener synthetic pathway.

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JULY 7-13, 2018 – VENICE

**Energy-Efficient Separation of Biomass-Derived, Hydrophilic Diols, Polyols and Monosaccharides from Aqueous-Phase by Adsorption on Functional Boronic-Acid Polymers**

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**Keywords:** Biomass, Separation, Adsorption

This study focuses on the development of an energy-efficient process for the recovery of biomass-derived, hydrophilic monosaccharides, polyols and vicinal diols from aqueous mixtures. Conventional separation techniques, such as distillation or extraction, are in most cases not applicable for separation of these compounds due to their low volatility, high boiling points and tendency to decompose at higher temperatures. Current industrial processes for separation are cost-intensive and energy-consuming, for example vacuum distillation and simulated moving bed chromatography.

Here we propose a method for selective recovery of compounds bearing a 1,2-diol structural motif from complex aqueous-phase solutions obtained after biomass processing. The method is based on the reversible esterification of the diols with boronic acids. Due to the dependency of equilibrium constant of esterification on the diol structure, the process is also applicable for separation of diols from each other. Separation of glucose from fructose presents a typical example based on a selective complexation of one isomer. An anionic liquid-liquid extraction process using molecular aromatic boronic acids has been already successfully implemented in our working group for recovery of fructose, xylulose, and 2,3-butanediol.[1-3] Considering the Principles of Green Chemistry, this process suffers, however, from disadvantages, such as use of an organic solvent along with utilization of quaternary amines as hazardous auxiliaries.

To overcome these disadvantages, aim of this research is the development of an adsorption process using cross-linked boronic acid polymers with high sorption capacity and sufficient stability. The current studies focus on radical polymerization of *p*-vinylphenyl boronic acid with various amounts and types of cross-linkers. Influence of the cross-linker on the sorption properties was observed. Introducing of at least 5 wt% of a cross-linker is required to ensure polymer stability, more than 40 wt% of cross-linker led to a decrease of sorption capacity. Most promising results are, for now, obtained using *p*-vinylphenyl boronic acid polymers cross-linked with either 20 mol% divinylbenzene or 20 mol% ethylene glycol dimethacrylate exhibiting sorption capacities of 341 and 221 mg fructose per gram polymer, respectively. These polymers were successfully tested for fructose recovery from a glucose-fructose mixture. Conversion of glucose into fructose is an important step for valorization of cellulosic biomass. However, the isomerization presents an equilibrium reaction and fructose recovery from the obtained mixture is challenging. Due to a higher complexation constant with fructose, this isomer selectively adsorbs on the polymer, whereas glucose remains in an aqueous solution. Fructose can be desorbed into an acidic solution.

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**Identification of novel biocatalysts from genomes of selected *Streptomyces* sp. soil isolates**

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**Keywords:** *Streptomyces* sp., biocatalysis, genome mining

Biocatalysis is application of enzymes and whole cells in synthetic chemistry and it is considered an environmentally friendly alternative to traditional metallo- and organocatalysis.[1] The need for innovative biocatalysts with improved or artificial properties is still present. One of the strategies to come up with the suitable biocatalyst is the search for new enzymes in the biodiversity using genome mining as an up-to-date approach for new enzymes discovery. Microorganisms are important source of novel enzymes for biocatalytic reactions and enzymes originating from *Streptomyces* are attractive because of their high stability and unusual substrate specificity.[2]

In our previous research we have functionally screened 118 *Streptomyces* isolated from the rhizosphere of plants and from mycorrhizosphere of fungi for 10 different industrially important enzymatic activities: ligning-peroxidase, laccase, cellulase, cutinase, tyrosinase, lipase, polyhydroxyalcanoate (PHA) depolymerase, gelatinase, proteinase and transaminase. Results showed that *Streptomyces* isolates from rhizosphere and mycorrhizosphere soils are “treasure troves” with high biocatalytic potential.[3]

The aim of our study was to identify novel biocatalysts from genome sequences of three selected *Streptomyces* sp. soil isolates, namely BV129, BV286 and BV333. De novo genome sequencing of 3 selected genomes was performed using standard next-generation sequencing platforms. Genome(s) assembly and gene annotation was performed using bioinformatics tools. Genome mining for the identification of genes coding for the aminotransferases and laccases was done using LAST tool. Sequence analysis retrieved 27 potential transaminases, while further analysis resulted three highly similar to previously described S-selective aminotransferase with high activity. Genome mining for laccase-coding genes resulted in 9 potential laccases, among them three highly similar to *Streptomyces* alkaline laccase previously described. Our results support the idea that *Streptomyces* genomes are useful source of novel enzyme-coding genes, high activity S-selective aminotransferases and alkaline laccases with potential industrial application.

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**JULY 7-13, 2018 – VENICE**

**Isolation and physicochemical properties of N-acetylglucosamine and glucosamine from pupae and adult Black Soldier fly waste.**

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**Keywords:** Black soldier fly, chitin, chitosan, degree of deacetylation, 13C NMR.

Black Soldier Fly (BSF) (*Hermetia illucens*) farming is gaining attention worldwide due to its effective waste management ability, protein and fat potentials and as a substitute for fish meal in poultry and aquaculture. However, wastes are produced during BSF farming. This waste could be used as alternative chitin source. This study, therefore set out to obtain value-added products, such as N-acetylglucosamine otherwise known as chitin and its derivative, glucosamine (chitosan) from the waste of both the pupae shells and adult South Africa BSF. Chitin was extracted through demineralisation, deproteinisation and decolouration processes and the resulted chitin was converted to chitosan by deacetylation process. The chitin and chitosan were characterised using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), cross polarisation-magic angle spinning nuclear magnetic resonance (CP/MAS-13C NMR) and Scanning Electron Microscopy (SEM). XRD analysis showed crystallinity index of 60.8 and 70.9% for adult and pupae chitin respectively. The degree of acetylation (96 for adult and 98% for pupae) was determined by 13C NMR. The materials were thermally stable at a temperature of 268 oC with a maximum degradation temperature (Tmax) of 391 oC and 384 oC for the adult and pupae respectively. Conversely, chitosan had reduced thermal properties with both stable at 220 oC and having Tmax values of 308 oC and 306 oC for adult and pupae respectively. This study revealed that both pupae and adult chitin, and chitosan have similarities in their physicochemical properties. With increasing investment in Black Soldier fly farming, chitin from this source could be an alternative to marine-based sources.

**New Methods for Isolation, derivatisation and utilisation of natural colorants**

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**Keywords:** Black chokeberry (*Aronia melanocarpa*), sustainable extraction, anthocyanins

Black chokeberry (*Aronia melanocarpa*) contains anthocyanins in high concentrations and has a simpler anthocyanin profile compared to other anthocyanin-containing berries. Aronia skin wastes used in this study were generated during the production of aronia's fruit juice. The batch method was compared with a new proposed method, namely an integrated extraction-adsorption and some extraction parameters were studied. The optimum conditions used for the batch method were as follows: extraction temperature of 60 °C, extraction time of 3 h, acid additive (0.1% v/v HCl), biomass-solvent ratio of 1:16 and biomass-SPE resin ratio of 1:1. An integrated extraction-adsorption was investigated to obtain higher anthocyanin yields. Higher anthocyanin yields were obtained when the process was performed for 3 h without cooling and the flow rate was 1.3 mL/s. Overall, a new proposed method showed a better anthocyanin yield and purity compared to a batch method by increasing the extraction yield up to about 20% and the anthocyanin content up to 40%. This method also simplified the process as three steps were eliminated during the process which eventually save more time and energy. Interestingly, the integrated method is also able to avoid any further degradation of anthocyanins during the extraction. Furthermore, an integrated extraction-adsorption method is an industrial scalable which potentially will be applied to produce a large quantity of anthocyanins. Anthocyanins present in *A. melanocarpa* skins were identified as cyanidin-3-*O*-galactoside (45.7%), cyanidin-3-*O*-arabinoside (16%), cyanidin-3-*O*-glucoside (3.6%), cyanidin-3-*O*-xyloside (2.7%) and the cyanidin aglycon (32%); cyanidin-3-*O*-galactoside and cyanidin-3-*O*-arabinoside were the major components. This is a particularly interesting observation as only one anthocyanin parent structure (cyanidin) and only monosaccharide glycosides were identified in the fruit, which is not typical compared to other berries which have a wider range of anthocyanins and/or more diverse glycosylation.

**Metaphosphates as Sustainable and Environment-friendly Electrode Materials for Sodium-ion Batteries**

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**Keywords:** Sodium-ion batteries, metaphosphates, sustainable and green batteries

To cope with the ever-increasing energy demand and significantly reduce CO<sub>2</sub> emissions, renewable and green energy sources such as solar, wind, tidal, biomass and geothermal, have been vigorously developing as alternatives to coal-fired plants for energy production.[1] These sources, however, are all inherently intermittent and widely dispersed. To make the best use of them, large-scale electrochemical energy storage systems (EESs) are required to store and moderate the power they produce to meet electricity grid requirements. By virtue of the abundance and easy accessibility of Na resources (*e.g.*, sea water) and similar electrochemistry to the well-established lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) have attracted the most attention as the candidate for construction of the large-scale storage stations. However, the jury is still out on the ultimate competitiveness of SIB versus other energy storage solutions, with one major uncertainty being a lack of Na electrode materials that perform as well as their Li counterparts in LIBs. Besides, with predictably huge demand for upcoming large-scale EES applications, stringent requirements on the cost effectiveness, materials sustainability, and environmental friendliness of the electrode materials in SIBs must be considered.

Inspired by the success of LiFePO<sub>4</sub>, phosphate materials with high safety and structural diversity have been extensively studied as SIB electrode materials. However, only a small number of compounds have been found so far that show same insertion mechanism as LiFePO<sub>4</sub>, and they are all either difficult to prepare or contain toxic transition metals (*e.g.*, V).[2] In our recent study, we found metaphosphate compounds that operate through conversion reactions are a promising way forward. A high reversible capacity of 150~300 mAh/g can be obtained after *in operando* crystal-to-glass transformation in the first discharge period from transition-metal (TM)(*e.g.*, Fe, Mn, Ni, Ti, Co, and Cu) compounds, and 50~150 mAh/g from main-group metal (MGM)(*e.g.*, Mg, K, Ca, and Al) compounds. Due to over-aggregation and separation of conversion products, which is caused by high capacity, TM metaphosphates show poor cycling stability; but NGM metaphosphates do not, due to their relatively low capacity. Making solid-solution materials (*e.g.*, Ca<sub>0.5</sub>Mn<sub>0.5</sub>) has therefore been proposed as, and demonstrated to be, an effective strategy to get better electrochemical performance from these materials as electrodes. These metaphosphate materials studied all are easy to make by conventional solid-state reaction routes, from environmentally friendly and sustainable metals like Al, Ca, Mn, Fe which are abundant elements in the Earth's crust. In this presentation, the structure characteristics, electrochemical performances, and working mechanism of these metaphosphate electrodes are discussed. Rietveld refinements against neutron powder diffraction (NPD) data reveal that these metaphosphates have ideal open framework structures with empty channels for ionic conduction. *Ex-situ* X-ray diffraction (XRD) and *in-situ* X-ray absorption near edge structure (XANES) data provide evidence for our understanding of the conversion reactions. These sustainable and environmentally friendly metaphosphate materials will be attractive and competitive electrodes for cheap, green and versatile large-scale stationary batteries.

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## NEW REACTION PATHWAYS

### Biomimetic halogenations at unactivated C-H bonds

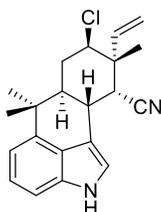
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**Keywords:** C-H activation, halogenation, abundant metals

Current halogenations at unactivated C-H bond are environmentally hazardous processes which require harsh reaction conditions and consequently occur with poor selectivity. On the contrary, enzymatic halogenations, carried out by the non-haem  $\alpha$ -ketoglutarate-dependent halogenases, occur at ambient temperature and under very mild conditions.<sup>1</sup> Harmless reagents are utilised and these reactions show extremely high selectivity. Taking inspiration from these enzymes, we propose that novel and more sustainable routes to carry out halogenating reactions can be developed.



**Fig. 1** Haliphanone G is a chlorinated natural product synthesised by a non-haem halogenases. C-H chlorination occurs at the end of the synthetic pathway.

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**JULY 7-13, 2018 – VENICE**

**Green synthesis of luminescent carbon quantum dots from coffee**

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**Keywords:** GO, FTIR, optical absorption, photoluminescence

The hydrothermal technique at low temperature was used to elaborate our nanoparticles (NPs) of graphene oxide (GO) from a natural Carbone source (coffee). FTIR confirm the different vibratory bonds of the elaborated GO. The optical absorption spectra show an absorption band located approximately at 270 nm which shift toward red for high concentration of GO dispersions. Photoluminescence spectra, shows a bathochromic emission, more intense for an excitation of 310 nm, and especially for low concentrations, gives a rise to an emission band situated at 407 nm. The results of the multi-exponential time decay gives a lifetime of:  $\tau = 4,07 \pm 0,03$  ns. The fluorescence of our Carbon NPs, shows their possible applications in the medical field.

**Metal-free transfer hydrogenation of azocompounds using a simple acyclic phosphite precatalyst**

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**Keywords:** Phosphite, Organocatalysis, transfer-hydrogenation

Transfer hydrogenation reactions are commonly catalyzed by precious-metal for which crustal abundance, expense, and toxicity are significant issues.<sup>1</sup> On the other hand, phosphites are widely used in catalytically active metal complexes, but they have very rarely exploited as catalyst themselves. In this work, the synthesis and characterization of the bulky tris(quinolin-8-yl)-phosphite, P(OQuin)<sub>3</sub>, (1) is described and its application as precatalyst in a metal-free transfer hydrogenation is studied. 1 promotes the dehydrogenation of H<sub>3</sub>N·BH<sub>3</sub> (AB) and reduction of symmetric/asymmetric azoarenes using AB as a H<sub>2</sub> source, obtaining really good yields (up to 95%). Mechanistic study suggests that 1 is act as a precatalyst as well as kinetic studies reveal (DKIE's) reveal that transfer of protic and hydride hydrogen from AB occur at the same time on the transition state of determined stage with  $\Delta S^\ddagger = -31$  e.u., being more likely than previous reported system. 2 In the frame of sustainable chemistry, systems like this fulfills at least 6 of 12 principles of the green chemistry.<sup>3</sup>

1.

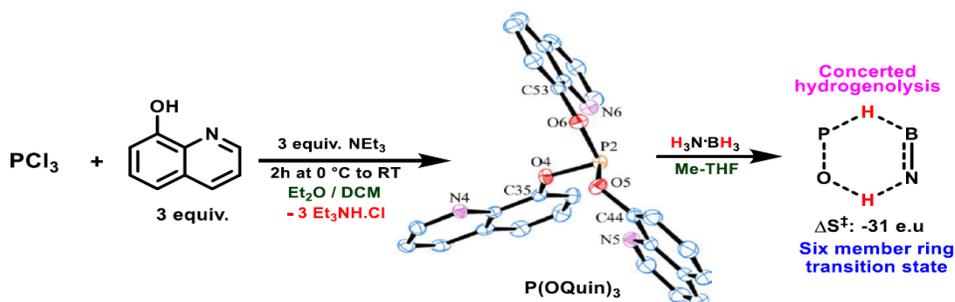


Figure 1. Synthesis of 1 and reactivity in from ammonia-borane.

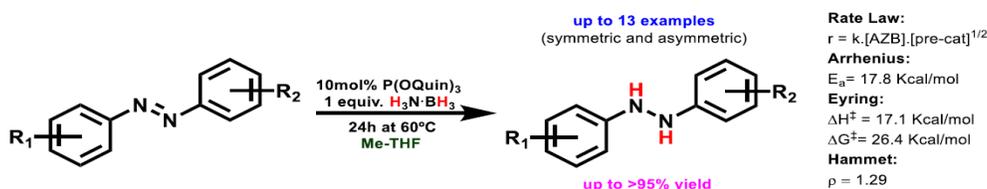


Figure 2. Optimized conditions for organocatalytic reduction of azoarenes and kinetics experimental values.

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**JULY 7-13, 2018 – VENICE**

**Silica supported sulfuric acid as a green catalyst for synthesis of symmetrical and unsymmetrical 1,2,4,5-tetraoxanes with good activity against Plasmodium falciparum**

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**Keywords:** Tetraoxanes, green methods, antimalarial

Tetraoxanes are endoperoxides that are novel scaffolds which have been synthesized as alternatives for artemisinin. These compounds have been exhibiting very good activity against Plasmodium falciparum, the most dangerous malarial parasite and which accounts half of all clinical cases. The synthesis of tetraoxanes has been a challenge because of low yield and use of very expensive catalyst such as rhenium oxide. So, the aim of this work is to synthesize 1,2,4,5 tetraoxanes from gem-dihydroperoxides using a cheaper and green catalyst. We found SSA as a green alternative for the synthesis of symmetrical (TS) and unsymmetrical (TU) tetraoxanes because it is reusable and cheaper. SSA can be easily made in the laboratory. The preparation of tetraoxanes involves the oxidation of an aldehyde or ketone to afford gem-dihydroperoxide (DHP) and condensation of DHP with another ketone or aldehyde to get the TU or condense the DHP itself to get the TS. So far, 8 compounds have been synthesized using SSA and 6 of them have been tested on Plasmodium falciparum and all presented good activity. The success of the synthesis was confirmed by NMR and IR spectroscopy.

**Synthetic route influence on the formation of supramolecular Co(III)-Mo(VI) double-complex salts**

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**Keywords:** solution-based synthesis, liquid-assisted grinding, cobalt polyoxomolybdates

The employment of different transition metal complexes and organic components along with polyoxometalates in the targeted synthesis and design of novel supramolecular materials having potential applications in the fields of heterogeneous catalysis and magnetism is of current trend in synthetic chemistry. The self-assembly of this inorganic-organic polyoxometalate based hybrids and their crystals formation is predominantly achieved by interplay of hydrogen bonding and electrostatic interactions.<sup>1,2</sup>

Our investigation<sup>3</sup> of the reactions between discrete anionic polyoxomolybdates and cationic *tris*(ethylenediamine)cobalt(III) complex, in the presence of malonic acid, resulted in a series of supramolecular Co(III)-Mo(VI) double-complex salts  $[\text{Co}(\text{en})_3]_2[\text{NaMo}_7\text{O}_{24}]\text{Cl}\cdot 9\text{H}_2\text{O}$ ,  $(\text{H}_3\text{O})[\text{Co}(\text{en})_3]_2[\text{Mo}_7\text{O}_{24}]\text{Cl}\cdot 4\text{H}_2\text{O}$ ,  $[\text{Co}(\text{en})_3]_2[\text{Mo}_7\text{O}_{24}]\cdot 5\text{H}_2\text{O}$  and  $[\text{Co}(\text{en})_3]_4[\text{Mo}_{22}\text{O}_{72}]\cdot 10\text{H}_2\text{O}$  (en = ethylenediamine). In order to explore the influence of the synthetic route on the formation of examined double-complex salts of Co(III) and Mo(VI), their synthesis was performed *via* both conventional solution-based methods (under room temperature or hydrothermal conditions), liquid assisted mechanochemical grinding (LAG) and aging method. To investigate the influence of the nuclearity of starting anionic polyoxomolybdates and role of malonic acid in these reactions,  $[\text{Co}(\text{en})_3]^{3+}$  macrocation was probed with  $[\text{MoO}_4]^{2-}$ ,  $[\text{Mo}_6\text{O}_{19}]^{2-}$ ,  $[\text{Mo}_7\text{O}_{24}]^{6-}$  and  $[\text{Mo}_8\text{O}_{26}]^{4-}$  in the presence and without malonic acid.

All compounds were characterized by means of infrared spectroscopy, thermal analysis and X-ray diffraction.

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The synthesis of substituted 6-((1H-1,2,3-triazol-1-yl)methyl)-5,6-dihydrothiazolo[2,3- c][1,2,4]triazoles by using click reaction

S.V.Grigoryan, A.S.Galstyan, T.V.Ghochikyan

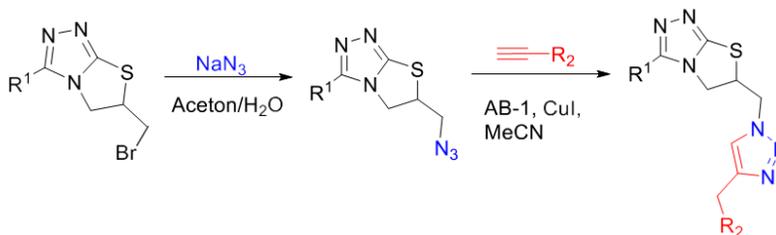
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**Keywords:** 1,2,3-triazole, 1,2,4-triazole, click reaction

Nitrogen contained heterocyclic compounds are very common in Nature, including amino acids, purines, pyrimidines, and many other natural products. One of the most interesting heterocyclic compounds is triazoles. They may have potential biological activities and there are various examples in the literature including anti-HIV activity, antimicrobial activity against Gram positive bacteria, selective adrenergic receptor agonist, etc.[1]. From another side the copper(I)-catalyzed union of terminal alkynes and organic azides to give 1,4-disubstituted 1,2,3-triazoles show remarkably broad scope and exquisite selectivity[2].

We tried to combine the biologically interesting groups into our system by using 1,2,3- triazoles as a linker molecule. For that reason the click reaction is used. Based on the conditions from the literature[3] we developed specific conditions for our system. We tried to keep all requirements of click chemistry.



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**Two-Step Continuous Synthesis of Dicarbonyl Indoles via I<sub>2</sub>/DMSO Promoted Oxidative Coupling: A Green and Practical Approach to Valuable Diketones from Aryl Acetaldehydes**

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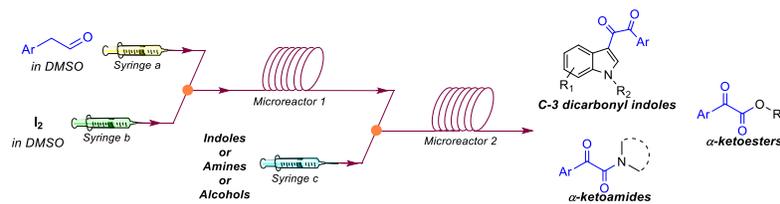
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**Keywords:** Continuous-flow synthesis, Diketones, Oxidative coupling

Indoles, a class of key structural element with biological and pharmacological activities, are prevalent in plenty of natural products, bioactive synthetic and functional materials. They also play an important role in drug development. Consequently, the research of further functional modifications of indoles is a hot topic in organic synthesis, which has attracted interest of chemists all over the world. Particularly, C-3 dicarbonyl indoles containing both indole and dicarbonyl structural units are powerful precursors for a variety of functional group transformations. Moreover, diketones such as  $\alpha$ -ketoamides and  $\alpha$ -ketoesters are also well known and useful structural moieties. Herein, A green and practical method for the synthesis of C-3 dicarbonyl indoles from aryl acetaldehydes and indoles was developed under I<sub>2</sub>/DMSO conditions, employing an assembled two-step continuous flow system. Moderate to good yields of dicarbonyl indole derivatives have been achieved by consuming lower dosage of iodine and shorter reaction time without amine catalysts added, which presents major advantages over reactions in traditional batch. Besides, this method was also compatible with the synthesis of  $\alpha$ -ketoamides and  $\alpha$ -ketoesters by adjusting the reaction parameters of continuous flow system, which indicates its good universality. And possible mechanism was proposed based on DMSO<sup>18</sup> isotopic labeled experiments.



- 35 examples up to 93%
- Readily available starting material under metal-free conditions
- High atom-economy
- Lower dosage of I<sub>2</sub> without amine catalysts
- Gram-scale continuous flow synthesis

Exploring organocatalysis for enantioselective carbon-carbon bond formation

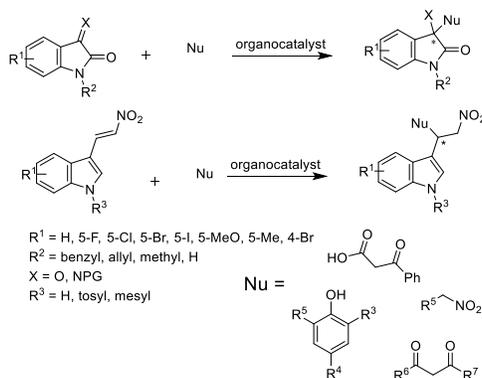
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**Keywords:** Organocatalysis, asymmetric, *Cinchona* alkaloids

Nature is a rich source of chiral molecules that can be used as chiral synthons, chiral resolving agents and chiral catalysts. In recent times, natural chiral molecules and their modified counterparts have been developed as chiral catalysts that can be employed for catalyzing variety of asymmetric organic reactions to obtain optically active molecules. This field of catalysis, which involves the use of small organic molecules as catalyst accessible from natural sources has been named as “Organocatalysis”,<sup>1</sup> the term coined by D.W.C. MacMillan. Organocatalysis received recognition and attracted great interest after the publication of two seminal research reports from the research group of Benjamin List and D.W.C. MacMillan.<sup>2</sup> Since then, this area of research has witnessed an impressive growth which has contributed to the discovery of new reactions under mild and ambient conditions. The organocatalytic reactions offer a rich platform for performing multi-component, tandem, or domino-type reactions, allowing the synthesis of structurally complex molecules in an enantioselective manner. This field of catalysis covers different kinds of organocatalysts such as chiral amines, thiourea, chiral phosphoric acids, *Cinchona* alkaloids and phase transfer catalysts, *etc.* In this context, we have successfully developed clean and green protocols for enantioselective synthesis of 3,3-disubstituted oxindole derivatives and 3-substituted indole derivatives (**Scheme 1**).<sup>3</sup>



**Scheme 1**

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Mild reductions of aldehydes utilising sodium dithionite under flow conditions

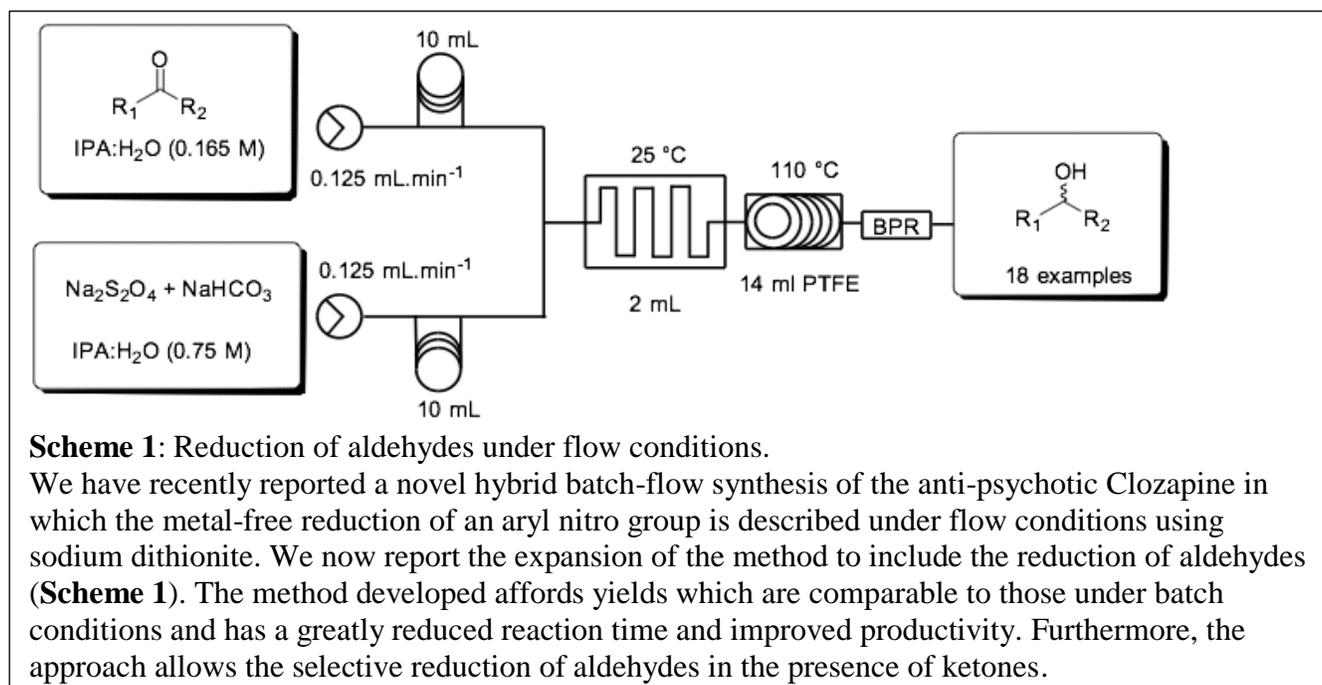
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**Keywords:** Flow Chemistry, Selective reductions, Metal free reductions



**Identification of novel biocatalysts from genomes of selected *Streptomyces* sp. soil isolates**

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**Keywords:** *Streptomyces* sp., biocatalysis, genome mining

Biocatalysis is application of enzymes and whole cells in synthetic chemistry and it is considered an environmentally friendly alternative to traditional metallo- and organocatalysis.[1] The need for innovative biocatalysts with improved or artificial properties is still present. One of the strategies to come up with the suitable biocatalyst is the search for new enzymes in the biodiversity using genome mining as an up-to-date approach for new enzymes discovery. Microorganisms are important source of novel enzymes for biocatalytic reactions and enzymes originating from *Streptomyces* are attractive because of their high stability and unusual substrate specificity.[2]

In our previous research we have functionally screened 118 *Streptomyces* isolated from the rhizosphere of plants and from mycorrhizosphere of fungi for 10 different industrially important enzymatic activities: ligning-peroxidase, laccase, cellulase, cutinase, tyrosinase, lipase, polyhydroxyalcanoate (PHA) depolymerase, gelatinase, proteinase and transaminase. Results showed that *Streptomyces* isolates from rhizosphere and mycorrhizosphere soils are “treasure troves” with high biocatalytic potential.[3]

The aim of our study was to identify novel biocatalysts from genome sequences of three selected *Streptomyces* sp. soil isolates, namely BV129, BV286 and BV333. De novo genome sequencing of 3 selected genomes was performed using standard next-generation sequencing platforms. Genome(s) assembly and gene annotation was performed using bioinformatics tools. Genome mining for the identification of genes coding for the aminotransferases and laccases was done using LAST tool. Sequence analysis retrieved 27 potential transaminases, while further analysis resulted three highly similar to previously described S-selective aminotransferase with high activity. Genome mining for laccase-coding genes resulted in 9 potential laccases, among them three highly similar to *Streptomyces* alkaline laccase previously described. Our results support the idea that *Streptomyces* genomes are useful source of novel enzyme-coding genes, high activity S-selective aminotransferases and alkaline laccases with potential industrial application.

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**In Situ EMR and DLS Studies of Liquid Phase Hydroxylation of Phenol to Dihydroxybenzenes in the Presence of FeO<sub>x</sub>/Siral Catalysts**

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**Keywords:** hydroxylation of phenol, FeO<sub>x</sub>/Siral catalyst, EMR, DLS

The mesoporous Siral type materials with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (1:1; 1:10 and 1:40) and immobilized FeO<sub>x</sub> structures were used as catalyst for direct hydroxylation of phenol to dihydroxybenzenes in the presence of hydrogen peroxide. The tested support materials (aluminous/siliceous) characterized with high surface area, well-defined regular structure and narrow pore size distribution of mesopores, and are suitable supports for the active components. Until today the nature of active sites and the mechanism of this reaction are discussed [1-3]. In the present report in situ and ex-situ electron magnetic resonance (EMR), and dynamic light scattering (DLS) are used to monitor the state of catalyst in liquid phase products of the hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> in the presence of FeO<sub>x</sub>/Siral catalyst. The magnetic properties and dispersity of the catalytic system as a function of duration of the reaction and temperature are monitored by EMR and DLS, respectively. The composition of reaction products is determined by Fourier transform infrared (FTIR) spectroscopy. The stable and intermediate magnetic species within room temperature - 343 K are identified. In the table dynamic light scattering data on the evolution of these liquid phase catalytic system are given. The nature of active sites are studied and the activity of the FeO<sub>x</sub> structures with superpara/ferromagnetic properties for this hydroxylation reaction based on the obtained data are discussed. Perhaps this is the first direct experimental evidence for in situ detection of nano- and micro-sized structures in catalytic systems for hydroxylation of phenol to dihydroxybenzenes in liquid phase. It was shown that in situ, real time monitoring of catalytic system by DLS provides useful information on the formation of particles and dynamics of their size and concentration in liquid phase and allows to evaluate the size of particles.

Table. DLS data on the catalytic system based on the FeO<sub>x</sub>/Siral catalyst (1 - the liquid solution of phenol in benzene; 2,3- the liquid phase catalytic system before and after reaction, accordingly)

Sample	Diameter of particles in liquid system, nm					Span	Diffusion Coefficient, E <sup>-13</sup> m <sup>2</sup> /s.
	Diameter for 10, 50, 90 % of particles			Mean	Mode		
	10	50	90				
1	1,7	2,2	2,7	2,1	2,3	0,52	3798,9
2	123,9	434,7	808,6	445,6	624,2	1,61	1,48
3	142,1	474,5	918,8	502,5	713,7	1,64	1,32

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## GREEN MATERIALS

### Study and the acid character of Molybdenum Oxide Supported on The zinc Orthophosphate catalysts: Use of isopropanol decomposition as test reaction

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In recent years, micro/nanomaterials have received widespread interest for application in areas such as luminescence, catalysts, sensors, energy storage and environmental fields, for the promotion of socio-economic development and improved environment and health care. One of the main reasons our attention focused on the preparation and study of phosphate-based nanomaterials. Preparation, textural and structural characterizations as well as acid properties of ZnPO<sub>4</sub> (Zn/P) (0.5; 1; 1.5) and since studies on this kind of catalysts are much fewer and its composition seems to lead to better acid characteristics. We have also focused our attention on catalytic activity and selectivity of Molybdenum oxide supported (MoZn/P). The (ZnP) used as a support was synthesized by coprecipitation and the catalysts MoZnP (5 wt %) was prepared by impregnation of ZnP with the ammonium heptamolybdate (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O. The morphology, porous texture, acid-base character and metal phase and dispersion, of these nanostructured materials were studied by several and complementary techniques; BET surface area measurement, X-Ray diffraction, transmission electron microscopy, scanning electron microscopy and Infrared spectroscopy, while their catalytic performance was assessed in the isopropanol decomposition. (nanospheres or nanofibers) was induced by fitting the surfactant ratios, being always obtained highly dispersed molybdenum nanoparticles on these nanostructures. The various ratios were tested in propan-2-ol decomposition calcined at various temperature, after pretreatment in situ under nitrogen stream in 200-340 °C temperature range. Their properties were compared with Mo/ZnP impregnated. The salts are active and the distribution of reaction products (propene, diisopropyl ether (DIPE) and acetone) depends both on the operating conditions and the catalyst composition. The improvement in acidity is mainly of the Brønsted acid type Mo/ZnP affects the structural properties of the pillared sample but gives a material with strong acid properties and both Lewis and Brønsted acid types are enhanced. It is reported also that textural and structural properties are not affected by the impregnation of a metallic function but the acid properties changed.

**Development of new phosphate glass fibers based on Moroccan natural phosphate for the reinforcement and amendment of the soil**

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**Keywords:** natural phosphate, clay minerals, phosphate glass, phosphate glass fibers, fertilizer, FX, OM, LD, SEM, tensile strength testing.

Morocco has 72.4% of the world's reserves of natural phosphate. It's the 3<sup>rd</sup> largest producer in the world (Manuel Frascati (2002)) and it occupies first place in the exploitation. However, the major part of this mineral is marketed in the form of raw materials with a much lower profitability than value-added products. To remedy this problem, several researchers have worked in the field of phosphate chemistry whose main applications are: glasses, biomaterials, materials with specific properties (optical, magnetic...)...etc. The object of our research was to propose a solution of the valorization of this mineral in its raw state, which takes into account economic, technical and environmental constraints.

For this purpose, the aim of our study was to develop new phosphate glass fibers for the reinforcement and amendment of the soil. In this work, we present our investigation related with the synthesis of new formulations of phosphate glass fibers based on natural phosphate and clay minerals.

Chemical composition, morphological, and mechanical properties of phosphate glass fibers have been investigated using various techniques such as: X-ray Fluorescence (FX), Optical Microscope (OM), Light Diffraction (LD), Scanning Electron Microscopy (SEM), and the tensile strength testing by traction machine. The elaborate fibers are characterized by their interesting mechanical properties, flexibility, homogeneity and transparency. The production of glass fibers based on natural phosphate opens numerous proposals for possible applications namely: in the field of agro-textiles, geotextiles, optical fibers, and for telecommunication...etc.

**JULY 7-13, 2018 – VENICE**

**Fe<sub>3</sub>O<sub>4</sub>-assisted oxidative polymerization of aniline**

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**Key words:** polyaniline, Fe<sub>3</sub>O<sub>4</sub>, biomimetic catalyst.

Conducting polymers are a special class of materials that possess properties of metals and semiconductors, while retaining good properties of polymeric materials such as easy processing. Polyaniline (PANI) is one of the most intensively studied electroconductive polymers due to its relatively simple synthesis, easily controllable properties, lightweight, good environmental stability, redox activity and wide range of electrical conductivity. It has become very attractive in many applications, especially in energy storage, electrochromic devices, sensors, antistatic coatings, radar-absorbing materials, etc.

In this study novel, eco-friendly method was developed for the synthesis of nanocomposites of PANI with magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles. Fe<sub>3</sub>O<sub>4</sub> was successfully used as a biomimetic catalyst for the oxidative polymerization of aniline. The reaction course was monitored by UV-Vis-NIR spectroscopy measurements which indicated the formation of electroconducting, polaron form of PANI emeraldine salt (PANI-ES). Isolated powdered nanocomposites were thoroughly examined by using a variety of different characterization techniques. Characteristic bands in FTIR and Raman spectra confirmed the presence of PANI in its emeraldine salt form, and EPR signal indicated the presence of unpaired electrons, which support the relatively high values of measured electrical conductivity ( $\sim 10^{-2}$  S·cm<sup>-1</sup>). Beside PANI reflections, X-ray diffractograms showed that the crystal structure of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in composites was preserved. Scanning electron microscopy revealed that the morphology of the obtained nanocomposites was, in major extent, controlled by the shape of magnetite nanoparticles. Based on the characterized properties, synthesised nanocomposites could be promising materials for energy storage and conversion applications.

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**Sustainable leather: methods and characterization**

Ghislain Rabodon

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**Keywords:** leather, chrome-free, characterization

The process to obtain leather from hides is called tanning. The tanning process involves a collagen stabilization using chemicals, in order to turn a putrescible pelt into a sustainable material. More than 90% of the leather is obtained with chromium sulphate. As a result, a high amount of heavy metal is present in waste water, leading to very expensive treatments for manufacturers. Some alternative products, like plant based polyphenol (tannin) can be employed in leather process, but such products react very slowly. Therefore, those products are incompatible with a fast tanning process required by large scale production. The third way to turn skin in leather employs organic reactants like formaldehyde or glutaraldehyde. Those chemicals can react very quickly but their drawback is a high toxicity for workers in tannery.

The aim of this project is to find new reagents that can turn raw skin into leather, without heavy metal and toxic aldehydes. In order to develop a new tanning process, several methods can be used to study and compare the efficiency of different tanning molecules. DSC can measure the denaturation temperatures of protein samples as an endothermic event on the spectrogram. An increase of the denaturation temperature implies a tanning effect of the reagent. Scanning Electron Microscopy can be an interesting tool to understand changes in leather structure during tanning process.

Leather organoleptic properties, like softness, are very important to evaluate the leather samples quality. In order to investigate the properties of the leather obtained with this new tanning process, tensile stress can be used as an indicator of the material softness. The higher the rigidity of the material, the higher the Young modulus of the leather is. As well, the breaking elongation tend to drop when the leather stiffness increase. Dynamical Mechanical Terminal Analysis is another technic useful to investigate the material properties before and after the tanning process.

**Innovative materials for membrane-based Green Chemistry development**

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**Keywords:** polylactic acid(PLA);eco-friendly solvent; flat sheet membranes.

Membrane technology can be considered as a sustainable separation process according to Process Intensification (PI) Strategy. In fact, it offer several advantages such as the possibility of integration with conventional technologies, low cost and energy reduction, safety and flexible scaling up [1]. However, the production of membranes via phase inversion, requires the use of toxic solvents and fossil-based polymers [2], which may have a significant negative environmental impact. In the present work, new sustainable materials, such as polylactic acid (PLA) as a biopolymer and methyl 5-(dimethylamino)-2-methyl-5oxopentanoate (Polarclean®) as new eco-friendly solvent, have been studied. In particular, membranes with two different structures (porous and dense) were prepared. The morphology, pore-size, mechanical properties and performance of the produced membranes, was then evaluated. A) PLA dense membranes The preparation and the characterisation of PLA dense membranes to be used in gas separation [3] was studied. Membranes were prepared by solvent evaporation-induced phase separation (EIPS). The effect biopolymer concentration and dissolution temperature on membrane properties, were investigated. The experiments in gas separation were realized under optimal conditions and the solution diffusion transport occurred. The experimental tests were carried out for single gases (He, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>). Permeance and permeability were calculated and the results showed that the membrane gave the best performance in terms of CO<sub>2</sub>/CH<sub>4</sub> selectivity (250). The CO<sub>2</sub>, CH<sub>4</sub> and other gases (permeability/selectivity) were plotted according to Robeson upper-bound [4]. B) PLA porous membrane using an eco-friendly solvent The porous PLA membranes were prepared using Polarclean® [5] as an eco-friendly solvent which demonstrated to be able to replace the most common traditional solvents generally applied in membrane preparation. Aim of this work was to produce totally sustainable porous membranes (having pore size in the microfiltration range) by vapour induced phase separation (VIPS) technique followed by immersion in a nonsolvent coagulation bath (NIPS). Preliminary water permeability tests were performed on the prepared membranes in order to evaluate their performances and their stability in time.

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## Bio-based Polymer

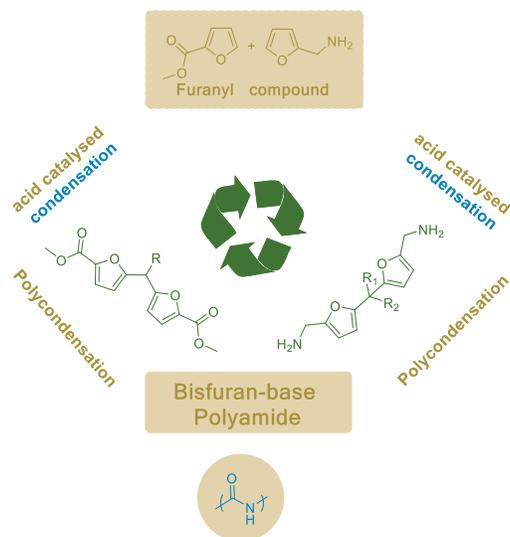
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**Keywords:** Bio-based; Polyamide; Bisfuran; Renewable

Motivated by the general concern about sustainability and environmental issues, an intense search for renewable-based polymers has grown exponentially in recent years. Discovery of renewable monomer feedstocks for fabrication of polymeric demand is critical in achieving sustainable materials. In the present work we have synthesized bisfuran diacid and bis furan diamine monomers from furanyl compound. The structures of these monomers were examined via <sup>1</sup>H NMR. Further, bisfuran diacid and bis furan diamine were reacted with aliphatic diamines and aliphatic diacid respectively, to generate bisfuran polyamide material. Furfural can be readily accessed from renewable and non-food-source biomass. The use of renewable furfural to access furan based polymer, would aid in generating next-generation bio-based materials. We have synthesized bisfuran diacid and bisfuran diamine monomers from furanyl compound to obtain the furan-based polyamides.



**Simple and efficient organocatalyst of guanidinium for ring-opening polymerizations of cyclic esters**

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**Keywords:** hydrogen bonding, organocatalysis, ring-opening polymerization

Organocatalyzed ring-opening polymerization (ROP) is a versatile approach to generate well-defined functional polymers. Typical organocatalyst promoted ROPs by activations of monomers or polymer chain ends via acidic or basic mechanisms.<sup>1-2</sup> Dual activating of both the monomer and the propagating polymer chain end clearly suggested an ideal strategy of widely tunable catalysis of high efficiency. Stoichiometric acid–base adduct was rarely employed in ROPs, since general acid and base usually quench each other into tight adducts. We propose that acid–base adduct may work bifunctionally in catalysis. The cationic part of the acid–base adduct as H-bonding donor (HBD) activated the monomer, and the counter anion part as H-bonding acceptor (HBA) activated initiator/chain end. A series of acid–base adducts were evaluated as catalysts in ROPs of lactide, carbonate, and lactone. Triazabicyclodecene chloride ([HTBD]Cl) exhibited excellent performances in the rate and control of ROPs of L-lactide (LA), trimethylene carbonate (TMC), and  $\delta$ -valerolactone (VL) with high conversions of 99%, predicted molecular weights from 2.83 to 20.86 kg mol<sup>-1</sup>, and narrow dispersity of  $\bar{D} = 1.07$ . Well-defined diblock copolymers consisting of PTMC, PVL, and PLA segments were synthesized. The controlled/living characteristics of the ROPs were verified by chain extension experiments. <sup>1</sup>H NMR, SEC, and MALDI-ToF MS analyses strongly indicated that the obtained polymers were exactly the designated ones. The bifunctional activation mechanisms were proposed and supported by NMR titrations. The experimental results indicated that acid–base adduct is competent organocatalyst in controlled/living ring-opening polymerizations.

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Tuning the H-bond donicity boosts carboxylic acid efficiency in ring-opening polymerization

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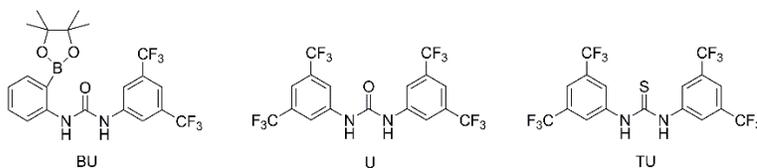
**Key words:** hydrogen bond; Brønsted acid; ring-opening polymerization.

**Introduction**

Hydrogen bond donor (HBD) binding with Brønsted acid (BA) catalyzed ring-opening polymerization (ROP) of cyclic monomers was developed.<sup>1</sup> Several groups made efforts to address H-mediated ROPs' critical shortcoming: low activity.<sup>2,3</sup> Our group designed internal Lewis pair enhanced H-bond donor (LPHBD): boronate-urea (BU) binding with the trifluoroacetic acid (TFA) as the catalyst to catalyze the ROP of the  $\delta$ -valerolactone (VL) and  $\epsilon$ -Caprolactone (CL)

**Results and Discussion**

Three ureas and thioureas (Scheme 1), four catalyst systems, TFA / TU-TFA / U-TFA / BU-TFA, were tested in the benchmark ROP. BU-TFA was the optimum catalyst system (Figure 1). We got the resulted polymers high molecular (PVL,  $M_{n,NMR}=2.51-9.92 \text{ kg mol}^{-1}$ ; PCL,  $M_{n,NMR}=2.51-11.1 \text{ kg mol}^{-1}$ ) and narrow dispersities (PVL,  $\text{Đ} \leq 1.16$ ; PCL,  $\text{Đ} \leq 1.18$ ). <sup>1</sup>H NMR, SEC, and MALDI-ToF MS analyses strongly indicated that the obtained polymers were the designated ones. The chain extension, kinetics experiments and the successful synthesis of the block copolymerization of VL and CL indicated the controlled/living nature of the catalytic ROP, and suggested the catalysis system is general applicable.



Scheme 1. Three urea and thiourea.

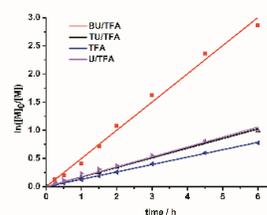


Figure 1. Semi-logarithmic kinetics plots

**Conclusion**

We presented an internal Lewis pair enhanced H-bond donor (LPHBD) binding with a Brønsted acid as the LPHBD-BA catalyst system for the living/controlled ring-opening polymerization of the cyclic lactones in solution at room temperature and improved the rate of polymerization. We believe that LPHBD will have more applications in the scope of ROP.

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**Integrated System of Forward Osmosis Membrane Process for Nutrient Recovery by Concentrating Anaerobically Digested Palm Oil Mill Effluent**

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**Keywords:** palm oil mill effluent, forward osmosis, cake filtration

Malaysia is known as the second largest palm oil producer with production of 17.32 million of crude palm oil (CPO) in year of 2016. The oil extracted from palm fruits can be manufactured into edible vegetable oil and biodiesel as renewable energy source. However, with the huge production of CPO, large volume of highly polluted wastewater known as palm oil mill effluent (POME) is produced. Excessive quantities of POME severely pollute the watercourse and disrupt the ecosystem. Due to the nature of POME with high chemical oxygen demand (COD) and biological oxygen demand (BOD), it is a suitable feed medium for anaerobic digester reactor to harvest methane in a form of biogas. This practice helps the palm oil industry to reduce the greenhouse gas emissions and carbon footprint. The digestate discharge from the reactor still remains a high strength wastewater with high nutrient content. Therefore, forward osmosis (FO) process, an emerging membrane technology, has the potential to recover the nutrients in the digestate. FO used the osmotic pressure difference as the driving force, results in concentration of a feed stream (agricultural effluent) and dilution of a highly concentrated salt stream. The nutrient rich-concentrated effluent will be reused as organic liquid fertilizer to the plantation. However, the presence of high suspended solids content in the digestate will cause membrane fouling issue and reduce the performance of FO process. Cake filtration has found to produce high filtrate quality by removing >80% of suspended solids from the digestate. The suspended solids removal is in the form of filter cake, which is considered as green waste that can be safely disposed or used for other purposes. The filter cake has been widely used as fertilizer in agricultural industry and also as structural soil conditioner in order to prevent soil erosion. Hence, an integrated system of FO process, which consist cake filtration process prior to FO, is found to be a novel approach for sustainable nutrient recovery in palm oil industry.

**Green microwave-assisted approaches for the synthesis of Nickel nanoparticles and for the design of Cu<sub>2</sub>S composites derived from wasted pig bristles**

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**Keywords:** Microwave chemistry, Nickel, Pig bristles

**Introduction**

Heterogeneous catalysis plays an important role in the production of more than 80% of all chemical products.<sup>1</sup> Therefore, the development of new heterogeneous catalysts via green and sustainable pathways is a captivating challenge. In the last decades, microwave-assisted reactions emerged as alternative reaction media due to associated advantages of the technique that include the possibility to obtain higher yields, different selectivities, as well as the potential to accomplish reactions/chemistries that generally do not take place under conventional heating conditions.<sup>2-3</sup> Herein, basing on our experience on microwave assisted techniques,<sup>4-5</sup> we show green approaches for the microwave-assisted preparation of pure metallic Nickel and copper sulfide carbon composites. Nickel nanoparticles have been successfully prepared from an environmentally friendly mixture of ethanol and ethylene glycol through an easy and fast microwave-assisted reaction.<sup>6</sup> The nanoparticles have been employed as catalyst for the hydrogenolysis of benzyl phenyl ether (BPE), a lignin model compound. The microwave assisted valorization of wasted pig bristles has allowed the preparation of photocatalytically active Cu<sub>2</sub>S carbon composites.<sup>7</sup>

**Methods**

For the preparation of magnetic Nickel nanoparticles, NiCl<sub>2</sub> was employed as metal precursor, while a balanced mixture of ethylene glycol and ethanol was simultaneously used as solvent and reducing agent. The best performance (71% yield) was achieved at 250°C in 5 minutes of microwave irradiation (CEM Microwave). The nanoparticles were analysed by Xray diffraction (XRD), scanning emission microscopy (SEM) and transmission electron microscopy (TEM) while the surface area was determined by nitrogen physisorption. The nanoparticles showed good activity in the hydrogenolysis of BPE, with a maximum conversion of 24%, and reusability up to 5 cycles without sensible lost of activity. Copper sulfide carbon composites derived from pig bristle were prepared by a new methodology employing ethylene glycol as solvent, pig bristle as sulphur and carbon source, and CuCl as metal precursors. The addition of different amount of NaOH favoured the formation of more photocatalytically active chalcocite crystals. The optimized conditions allowed the preparation of Cu<sub>2</sub>S composites in 4 minutes at 200°C, using an ETHOS Microwave. The composites were successfully prepared and characterized by XRPD and SEM. Cu<sub>2</sub>S carbon composite showed photocatalytic properties for the degradation of methyl red, a pollutant dye, under visible light irradiation, reaching ~40% of degradation in 3 hours under visible LED light irradiation.

**Acknowledgments**

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## REACTION MEDIA

### A green bioprocess for the synthesis of flavour esters in Sponge-Like Ionic Liquids

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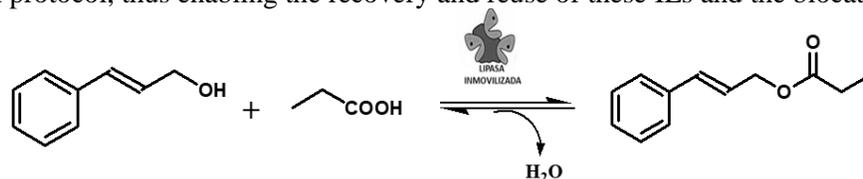
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**Keywords:** Cinnamyl esters, Ionic Liquids, biocatalysis process

The background of Green Chemistry consists in the design of more sustainable processes, by improving the efficiency of transformations and by preventing the use and generation of dangerous substances or transform those that are already generated into less dangerous compounds.

In this context, Sponge-Like Ionic Liquids (SLILs) are hydrophobic ionic liquids based on alkyl cations with long side chains that change from liquid to solid state with temperature. Due to their properties, SLILs have been proved to be excellent solvents, generating monophasic reaction media at compatible temperatures with enzymatic catalysis [1,2]. Therefore, due to the switchover nature of these SLILs, it has been possible to design a sustainable separation-reaction protocol, thus enabling the recovery and reuse of these ILs and the biocatalyst [3].



**Figure 1.** Synthesis of cinnamyl propionate catalyzed by an immobilized lipase.

Cinnamyl esters have many applications in food, cosmetic and pharmaceutical industries due to their aromatic properties [3]. This work describes a sustainable biocatalytic process for the synthesis of cinnamyl esters using SLILs (Bis [(trifluoromethyl) sulfonyl] imide trimethylhexadecylammonium [C<sub>16</sub>tma] [NTf<sub>2</sub>]) and immobilized *Candida antarctica* lipase B as biocatalyst (Figure 1). The genuine properties of SLILs allowed to carry out the separation of the flavour products by a straightforward protocol that permits the full recovery of the SLILs/biocatalyst system for reuse.

#### Acknowledgments:

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**Levulinate Ionic Liquids: an efficient and sustainable platform for cellulose processing**

Andrea Mezzetta, Stefano Becherini, Cinzia Chiappe, and Lorenzo Guazzelli,

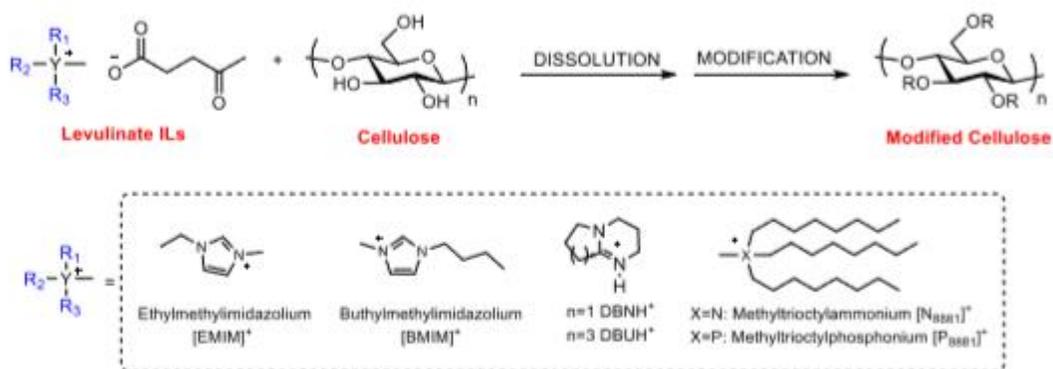
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**Keywords:** cellulose, ionic liquids, dissolution

Cellulose is the most abundant renewable polymer on earth,<sup>1</sup> for this reason a lot of efforts have been spent to transform cellulose into smaller valuable molecules (for instance levulinic acid)<sup>2</sup> and other modified useful polymers.<sup>3</sup> However, derivatization processes are limited by the poor solubility of cellulose in most solvents. Therefore, the solubilization and use of cellulose represent a challenge for a more sustainable future. In the last 15 years, ionic liquids (ILs) have been used as new solvents for cellulose, and they have proven to be very useful in cellulose chemistry, including its derivatization.<sup>4</sup>

We synthesize, through an easy, high yielding and clean procedure new levulinate-based ionic liquids. These ionic liquids were characterized (NMR, TGA, viscosity) and their cellulose dissolution ability was tested. For each IL, we tested different temperatures (40-100 °C). The dissolved cellulose was regenerated by addition of an anti-solvent and analyzed (TGA, FTIR) and the IL was recycled and reused without any appreciable decrease of its dissolution ability. All the ILs demonstrate an unexpected dissolution power. In particular, EMIMLev is able to dissolve high amount of cellulose at 100 °C. The obtained ILs-cellulose solutions were successfully used to perform unprecedented reaction on the dissolved cellulose.



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**Deep Eutectic Solvents as versatile solvents. From their properties to their applications**

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**Keywords:** Alternative solvents, eutectic solvents, properties/applications

Eutectic solvents have been known for a long time, but the term Deep Eutectic Solvents (DES) was coined by Abbott et al., referring to mixtures formed between quaternary ammonium salts and hydrogen bond donors<sup>1</sup>. DES are simply formed by mixing the compounds, usually a hydrogen bond donor and an acceptor, in an appropriate molar ratio. The solid compounds become liquid at room temperature, due to the interactions established between the DES constituents (usually hydrogen bond interactions), which render a mixture with a melting point much lower than that of the individual compounds. Choline chloride (ChCl) and urea, glycerol and ethylene glycol are known to form DES, as well as some carboxylic acids<sup>3</sup>. When the DES are formed between primary metabolites such as amino acids, organic acids and sugars, they can also be called natural deep eutectic solvents (NADES)<sup>4</sup>. They can even be formed from therapeutically active species<sup>5</sup>. Since then, these solvents have received a lot of attention from both academic and industrial sectors, especially owing to its versatility, simple production and low price. They have already found uses in electroplating applications, as extraction solvents<sup>6</sup>, as solvents for biocatalyzed reactions<sup>7</sup>, for CO<sub>2</sub> solubilization and gas separations<sup>8</sup>, among others. Nevertheless, at the same time these solvents became more and more popular, the lack of information on their fundamental properties (thermodynamic, structural, etc.) became more evident. There is the need to rationalize DES's properties with its possible applications, mainly the thermal behavior, rheological properties, polarity, water content and conductivity. This work presents some of the thermophysical properties of DES and NADES, and also explores some of their applications in the fields of materials processing, biocatalysis and extraction.

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JULY 7-13, 2018 – VENICE

**(Eco)toxicological and Antibacterial Effects of 24 L-Phenylalanine Derived Ionic Liquids against Marine and Clinically Relevant Bacteria**

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**Keywords:** ionic liquids; (eco)toxicity; bacteria

A series of 24 ionic liquids (ILs), containing a phenylalanine, a diverse of cations and alkyl chain lengths (C<sub>2</sub> to C<sub>16</sub>), was screened for their toxicity and antibacterial activity toward three bacteria; *Vibrio fischeri*, *Staphylococcus aureus*, and *Escherichia coli*. For that purpose ISO 213338:2010 (bacterial bioluminescence inhibition assay for *V. fischeri*; 30-min EC<sub>50</sub> and 4-h MBC) and ISO 20776-1:2006 (bacterial growth inhibition assay for *S. aureus* and *E. coli*; 20-h MIC and 20-h EC<sub>50</sub>) was conducted. The main influence was seen to be performed by the alkyl chain length and “cut-off” effect (toxicity could not increase any further in a certain chain length). The results showed that elongation of alkyl chain followed the trend of increased toxicity until C<sub>12</sub>. The EC<sub>50</sub> values ranged from 8 (C<sub>12</sub>) μM, 4 (C<sub>12</sub>) μM, 16 (C<sub>12</sub>) to > 2000 (C<sub>2</sub>) μM for *V. fischeri*, *S. aureus*, and *E. coli*, respectively. Values of 4-h MBC were on average up to 10 fold higher compared to 30-min EC<sub>50</sub> values of *V. fischeri*. For 20-h MIC of *S. aureus* and *E. coli* were on average from 1.5 to 3 fold higher compared to 20-h EC<sub>50</sub> values. The toxicity results also indicated that *V. fischeri* bioluminescence inhibition assay proved more sensitive to the toxic effects of ILs than *E. coli* and *S. aureus* growth inhibition test.

**Acknowledgements:** Authors would like to acknowledge European Union's Seventh Framework Programme for Research, Technological Development, and Demonstration under Grant Agreement no. 621364 (TUTIC-Green), Estonian Research Council grant PUT 1656 and IUT 23-5, and “TTÜ arenguprogramm aastateks 2016-2022” Graduate School in Biomedicine and Biotechnology“receiving funding from the European Regional Development Fund under program ASTRA 2014-2020.4.01.16-0032 in Estonia.

**Fe-based magnetic ionic liquids: Synthesis, characterization, and application for carbon dioxide fixation**

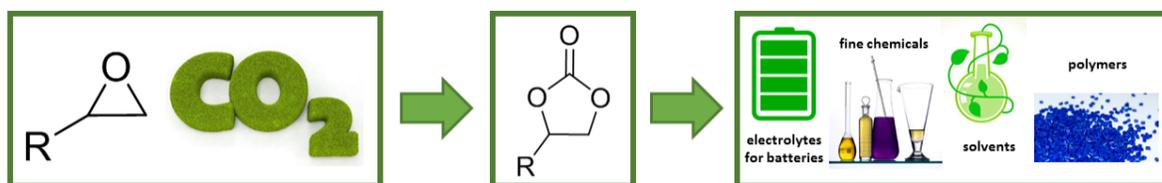
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**Keywords:** ionic liquids, catalysis, carbon dioxide fixation

The use of carbon dioxide (CO<sub>2</sub>) as a C1 building block is a very attractive process as it is abundant, non-toxic, non-flammable, and cheap. However, a lot of energy is needed for the activation of CO<sub>2</sub>, due to the oxidation state of carbon.<sup>1</sup> Metal containing ionic liquids have recently shown good prospect as catalysts for the formation of cyclic carbonates through the fixation of CO<sub>2</sub> in epoxides.<sup>2</sup> In addition to their catalytic properties, metal containing ionic liquids show interesting properties like, response to an external magnetic field and this can be used for new possible applications for magnetic and electrochromic switching, such as transport and separation of materials, separation of greenhouse gases, magnetic surfactants and more.<sup>3</sup>



Herein, we describe the synthesis, characterization and catalytic applications of a well-defined imidazolium based iron-containing ionic liquid [BMImFe][(NO)<sub>2</sub>Cl<sub>2</sub>]. Such a characterization enabled us to establish the actual structure of the iron-based containing IL, which was found to be an active catalyst for the cycloaddition of CO<sub>2</sub> to epoxides, giving high conversions for various substrates under near ambient conditions. The complex works as a bifunctional catalyst without the need of any additive or co-catalyst, in which the metal centre plays a role as Lewis acid and the chloride anion, as part of the [BMIm][Cl] moiety, acts as nucleophile.

The reaction mechanism and the nature of the different species involved in the catalytic cycle of this transformation were investigated by experimental studies. Such experiments demonstrated that the imidazolium moiety is involved in the catalytic process, whereas the reaction proceeds with retention of configuration through a nucleophilic attack to the C<sub>1</sub> of epoxide. In addition, kinetic studies showed that the process followed first-order kinetics regarding epoxide concentration and revealed the presence of a fast pre-equilibrium in which the iron-containing ionic liquid [BMIm][Fe(NO)<sub>2</sub>Cl<sub>2</sub>] (non-reactive state) dissociates at high temperature and generates the true-catalytically active species, [BMIm][Cl] + [Fe(NO)<sub>2</sub>Cl]. On the basis of these experiments, a catalytic cycle was proposed.

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**JULY 7-13, 2018 – VENICE**

**Ionic liquid catalysts for glycolysis of PET**

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Polyethylterephthalate (PET) is a ubiquitous material, it is predominantly used for bottles, packaging, clothing and carpets. This generates non-biodegradable waste, considering 11% of household waste is plastic, 40% of which is plastic bottles, a solution to this is required. Recycling is the obvious approach, unfortunately most post consumer PET recycling is physical. Physical recycling produces lower quality polymers that is used for fleeces and carpets, additional concerns regarding contamination make physical recycling inappropriate for use with food packaging. Unlike physical recycling; chemical recycling regenerates the monomer allowing for the production of pristine high quality polymer. The transesterification reaction between ethylene glycol and PET produces bis(2-hydroxyethyl) terephthalate (BHET), a monomeric intermediate in PET production, which is easily converted to PET. Catalysts tested for this reaction were imidazolium based ionic liquids, most studies in literature utilising ionic liquids to-date incorporate metal salts, in particular ZnCl<sub>2</sub> and CoCl<sub>2</sub>. These ionic liquids were produced by combining [bmim]Cl with the metal salt in a ratio of 2:1. These catalysts were very effective for the transesterification reaction, achieving over 89% yield using [bmim][ZnCl<sub>4</sub>] or [bmim][CoCl<sub>4</sub>]. Through the work presented here it was seen that imidazolium acetate ionic liquids can be effective catalysts for glycolysis of PET without addition of metal salts, achieving greater yields than the chlorometalate ionic liquids tested under equivalent conditions. Through modification of the cation it was found that capping the C2 position on imidazolium cation lead to no conversion, this suggests that in-situ carbene formation may be an important part of the mechanism. The modification of the cation also showed that steric bulk had a large impact on yield, future work on the cation will investigate the impact the electronic structure has. Some work has been done on diimidazolium ionic liquids this will also be followed up on by modifying the backbone of the cation, with a particular focus on enhancing rigidity and reducing steric hinderance

**Sponge-like ionic liquids as an efficient tool for green chemical processes**

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**Keywords:** Sponge-like Ionic liquid, green process, biocatalysis

Ionic liquids (ILs) are solvents entirely composed of ions. Because of their nature, ILs exhibit very interesting properties like low melting point (under 100°C), low volatility, and thermal stability, which make them non-hazardous solvents. Besides, the feasibility of tuning their physical-chemical properties through the election of cations and anions, have opened a door to their application in many areas in chemistry and industry. Data reported by Dupont [1] and Lozano [2] reveal that ILs are able to accommodate other molecules (like substrates and products), and even macromolecules, like active biocatalysts in their ionic net thus creating homogeneous reaction media. Replacement of conventional catalysis by biocatalysis ensure a higher efficiency in specificity under softer conditions of energy demand, in accordance to several principles of Green Chemistry (Energy efficiency, Prevent Waste, Atom economy, Reduce derivatives, and Catalysis vs. Stoichiometric) [3]. This explains why ILs have emerged as the perfect non-aqueous reaction media to develop green biocatalytic processes, where due to the low volatility of ILs is feasible their recovery and reuse together with the biocatalysts.

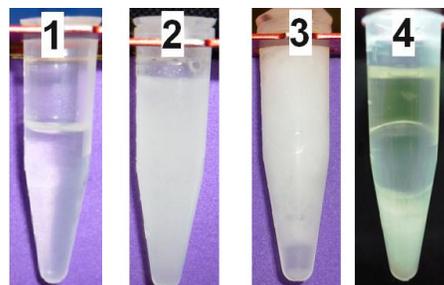
Sponge-like ionic liquids (SLILs) are a group of hydrophobic ILs with long alkyl side chains that provide an extra feature to integrate the synthesis and purification steps into a green approach. Their nanostructured organization allows the incorporation of substrates and products within the gaps of the ionic matrix and the later expelling by compaction of the gaps, in function of the temperature [4].

This strategy was firstly described for the synthesis of flavor esters [4], and later was successfully applied for the production of biodiesel [5] and monoacylglycerides [6].

All these processes share two important goals:

Firstly, the resulting increased yield and specificity on the biotransformation because of the genuine solvent properties of SLILs, which provides an improved catalytic efficiency on the enzyme action.

Secondly, a green protocol for product purification and SLIL-biocatalysts recovery for reuse. This protocol, which does not involve the use of VOCs, consists on iterative centrifugations at low temperatures (against traditional distillation) which results energetically economic.



**Figure 1.** Purification of methyl oleate and glycerol obtained by Novozym 435-catalyzed methanolysis of triolein in SLIL. (1). Homogeneous reaction media at 60°C, (2) 60°C after addition of water, (3) the SLIL turns solid at 25°C, and (4) separation of three phases after consecutive centrifugations at controlled temperatures [5].

**Acknowledgements:**

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**Solvent-free synthesis of  $\gamma$ -valerolactone from biomass-derived levulinic acid by arene Ru<sup>II</sup> and Ir<sup>III</sup> pre-catalysts**

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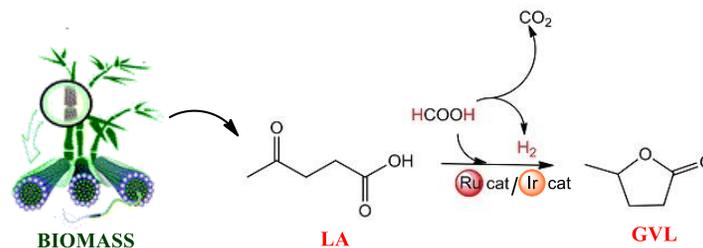
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**Keywords:**  $\gamma$ -Valerolactone, Solvent-free, Recyclable catalysts

The sources of carbon for the production of fuels and chemicals have for the past century been derived from fossil resources (coal, crude oil and natural gas). However, burning of these fossil products causes environmental pollution and also has a great impact on the climate. To avoid these problems, which are of great concern to the world at large, scientists are looking towards the utilization of alternative sources of carbon for the production of these fuels and chemicals. Plant biomass is one of such important alternative sources of carbon. Carbohydrate polymers in plant biomass can be transformed into many chemicals including ethanol, n-butanol, sorbitol, furfural, 2,5-hydroxymethylfurfural and levulinic acid (LA). In turn, levulinic acid can be converted into  $\gamma$ -valerolactone (GVL), which is one of the most promising renewable platform molecules. GVL can be transformed into various chemicals including, 1,4-pentanediol, 2-methyl tetrahydrofuran and 2-butene, and also serves as an intermediate in the production of various biofuels as well as commodity and fine chemicals. Herein, we report selective and efficient solvent-free hydrogenation of levulinic acid (LA) into  $\gamma$ -valerolactone (GVL) (Scheme 1) by new pyridinyl-imine ruthenium(II) and iridium(III) complexes as catalyst precursors.

**Scheme 1:** Synthesis of bio-derived  $\gamma$ -valerolactone



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## ANALYTICAL CHEMISTRY & GREEN CHEMISTRY FOR RESTORATION

### Selective adsorption of thiophene and its polyaromatic derivatives from fuels by bioadsorbent: a study of equilibrium

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**Keywords:** desulfurization; bioadsorbent; equilibrium

The intense oil production worldwide leads to depletion of old and commissioning of new oil fields comprising increasingly high sulfur quantity. Polycyclic aromatic derivatives of thiophene, which have been passed into the industrial and automotive fuels lead to emissions of sulfur oxides, with all the resulting harmful effects on the environment and human health. Among the alternative methods for the purification of fuels, particular attention is paid to the method of adsorptive desulfurization, which is based on the selective adsorption of the organic sulfur compounds from the fuel onto solid adsorbents. From this point of view the processing of the rice husks waste in order to obtain materials, suitable for adsorptive desulphurization of fuels, is of interest.

In this work the adsorption affinity of pyrolyzed rice husks (PRH) toward thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) was studied in single and mixed solutions. Adsorptive desulfurization was investigated using model fuel as well as real diesel, in batch mode. A relatively high adsorption capacity of the PRH, more than 40% is observed at low initial sulfur concentrations in the fuel, up to 1000 ppm. The adsorption activity of the PRH was evaluated in terms of correlation between their structural characteristics and surface chemistry. The adsorption selectivity of the PRH from single solutions of the three aromatic sulfur heterocycles (ASHs) decreases in the order T>BT>DBT. The theoretical equilibrium adsorption capacity of PRH in regard to adsorption of the three sulfur compounds from model fuel and commercial diesel was determined using the adsorption isotherms of Langmuir, Freundlich, Dubinin–Radushkevich and Temkin. The values of the coefficients of determination as well as standard deviation revealed that the adsorption of T, BT and DBT from model fuels by PRH is described adequately by the isotherms of Freundlich and Langmuir. The statistics of the two isotherms show that the standard deviations for Freundlich are much smaller and the results are uniformly distributed, therefore, this model more adequately described the adsorption equilibrium. The adsorption of T and DBT from model fuel on pyrolyzed rice husks, under the specified experimental conditions is also well described by Temkin isotherm. The calculated values for the equilibrium heat of adsorption, are low which is usually associated with predominantly occurrence of physical adsorption. The adsorption of T, BT and DBT from mixed solutions, according statistical data is satisfactorily described by the Freundlich, Langmuir and Temkin isotherms. These results revealed that the simultaneous adsorption of ASHs with PRH obviously takes place with the participation of both, non-specific and specific interactions between adsorbent and adsorbate.

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**JULY 7-13, 2018 – VENICE**

**Nylon 6/octadecylsilane composite, as a thin film microextraction sorbent for the determination of Bisphenol A in water samples**

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**Key words:** Thin film microextraction, Bisphenol A, Water samples

Here we report a simple, rapid and reproducible method for a novel composite fabrication following by its application in Thin Film Microextraction (TFME). Nylon 6 (PA6) was dissolved in formic acid and combined with octadecylsilane (C18) and polyethylene glycol by sonication, then the mixture was poured on a Petri dish and was kept in room temperature. After solvent evaporation, the dried thin film composite was cut in house shape form and attached to a TFME extraction setup. To examine the extraction potential of the prepared composite, Bisphenol A (BPA) was used as the analyte.

BPA is an endocrine disrupting compound with high applicability in polycarbonate plastics (like baby bottle) and epoxy resin production (like food cans). Annually, over one million tons of BPA are produced all over the world which can cause a great concern for human health. So it is important to investigate BPA in concentration levels below 50 µg/Kg (a reference dose determined by Environmental Protection Agency (EPA))

In the following, TFME setup was performed and High Performance Liquid Chromatography (HPLC) with UV-detection was applied for the analysis. To optimize extraction efficiency, three other sorbents including Lichrolut En, nanoclay and multiwalled carbon nanotube were also combined with PA6 and fabricated with the same procedure. Afterward, the extraction efficiency of all prepared composites were investigated and C18-PA6 showed the highest enrichment factor (30.6). After optimizing experimental parameters affecting extraction (like extraction time, desorption condition and etc.), the detection limit, dynamic range and relative standard deviation of the method at two concentration level of 2.0 and 800 µg/L was obtained to be 0.8, 1-1000 µg/L and 6.9% , respectively. Finally, four real samples including polycarbonate baby bottle, river water and waste water samples were analyzed by the method.

**JULY 7-13, 2018 – VENICE**

**Adsorption Study Of Organic Pollutants On Carbonaceous Sorbents**

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**Keywords:** POPs (persistent organic pollutants), activated carbon, pollution, soil

Problems associated with decontamination of polluted sites showed the necessity to develop remediation technologies that are practical, fast and deployable in a wide range of physical conditions. In response to the growing need to address environmental contamination, many technologies have been developed for the treatment of in situ and ex situ soil remediation such as dig and dump, soil vapor extraction, thermal treatment and bio-remediation.

The aim of this paper is to study methods and approaches for remediation from certain organic pollutants with sorbent use.

The origin of organic pollutant compounds in soil is from uncontrolled burning of various wastes, incomplete combustion, as well as the uncontrolled dispersal and from transport units used in agriculture. From soil, pollution reaches the surface or ground water and as we use it a lot, it has a negative impact on our health.

Improvement with activated carbon (AC), to reduce exposure to contaminated soils and sediments has recently become a promising remediation process. Most studies not only on sediments and on soils were conducted in the laboratory and only few in the field. The practical experience on land scale is scarce and achievable approaches with activated carbon amendment needs to be developed, especially for soils.

Activated carbon reduces successfully the bioavailability of organic contaminants because of its strong sorption properties.

First, being an in-situ technique it is more cost-effective compared to the ex-situ remediation and it is environmental friendly because contamination problems are not moved from one place to another.

Secondly, being properly applied it does not release new quantities of pollutants as it could be in case of dredging or digging. On the third hand, sometimes it is more effective than for example purification with surfactants or other chemicals (in or ex situ) or phytoremediation.

Once pesticides are adsorbed onto activated carbon, they become biologically inactive and cannot cause damage to grass.

The major advantage that concerns our country is that currently activated charcoal began to be a local product; it is obtained by a technology proposed by the team of researchers of the Institute of Chemistry, Republic of Moldova.

**JULY 7-13, 2018 – VENICE**

**Technology of extractional method of refining the waste waters polluted by diesel fuel and investigation of some physical- chemical aspects of the extractional process**

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**Keywords:** technology of refining the waste waters, polluted by diesel fuel, liquid –phase extraction with organic solvents, kinetic and physical –chemical properties of extraction process.

There has been worked out the technology of liquid –phase extraction with organic solvents on refining the waste waters polluted by the products of oil recycling – a diesel fuel.

The physical – chemical aspects of the extraction process have been established. The results of kinetic and recycling calculations for apparatus get up the extraction junction on refining the waste waters.

**JULY 7-13, 2018 – VENICE**

**Spent coffee grounds as a green source of highly active carbon sorbents**

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**Keywords:** Requalification of spent coffee grounds, Production and characterization of activated carbon, Activated carbon adsorption

The coffee production amounted to approximately 159 million of 60 kg bags worldwide in 2012-2013, with the consequent formation of a similar quantity of residues and waste during the whole material life cycle, from the harvesting to the brewing. Furthermore, the consumption demand is increasing year by year. According with the directive 2008/98/EC, the waste production should be minimized through reuse and recycle, reducing the burden of waste management and disposal. This approach is useful to gain a circular economy and it could be improved by political incentives and by increasing the economic value of the waste. Based on these perspectives, the research project is focused on the conversion of spent coffee grounds, coming from different brands, into highly active porous sorbents by mean of pyrolysis. The treatment process was tested at different experimental conditions to obtain the best yield in terms of BET and adsorption capacity. Moreover, the pyrolysis was performed changing one parameter time by time, in order to understand the influence in the process of the temperature, the typology of inert and the related flow rate, the reagents' dosage and the holding time. The initial coffee mass and the temperature ramp (10 °C/min) were kept constant for each experiment. At the end of the thermal treatment, each sample was washed with the same amount of deionized water until neutral pH and dried in oven at 105 °C. The obtained activated carbon was characterized by different microscopy and spectrophotometric techniques (i.e. ESEM, Raman, XRD, XPS, solid <sup>13</sup>C NMR) together with the BET analysis, with the purpose to determine its physical and chemical nature. Finally, the adsorption capacity of each sample was evaluated for different pigments: methylene blue (cationic), erythrosine-b (anionic) and bromothymol blue (non-ionic). Their initial concentration and the amount of activated carbon used in the test were arbitrarily set. A fixed volume of pigments' solution (100 ml) underwent adsorption and the concentration changing in time was evaluated with a UV-VIS spectrophotometer. Two different commercial activated carbons were analyzed as reference. They are commonly used for the treatment of potable water and wastewater, in particular for the removal of mobile persistent organic contaminants.

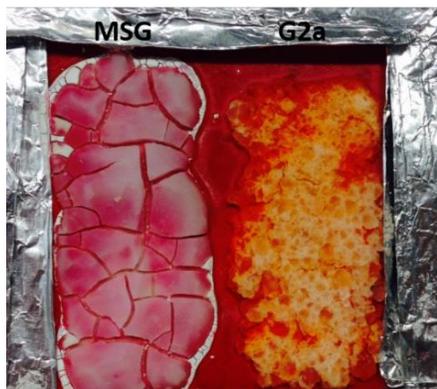
## Silica Sol-Gel Chemistry & Dimethylcarbonate: A Sustainable Approach To Graffiti Removal

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A novel series of two-component systems suitable for removing graffiti and murals from historic building, masonries and stone artworks has been developed. New systems have been achieved through a low-environmental impact and cost-effective methodology by combining silica sol-gel chemistry and dialkylcarbonates chemistry.<sup>1,2</sup>



**Figure 1.** Gels application over aerosol spray painted Istrian stone samples.

Silica gels were synthesised in basic conditions by using ethylene and propylene glycols as organic co-solvents.<sup>3</sup> These gels represented the solid absorbent hybrid matrixes, dimethyl carbonate (DMC) was load into as the green organic solvent. An *ad hoc test tube* methodology was conceived for preliminary

assessing new systems efficiency in extraction/trapping the components of commercial red aerosol spray paint. The lead products resulting from this test were evaluated on mock stained samples of Istrian stones (Figure 1). Visual inspection, NMR spectroscopy and FT-IR spectroscopy provided the necessary information, in order to identify the most promising cleaning agent of this series paving the way to its full characterisation and features improvement. Moreover, the data collected confirmed the validity of the proposed approach to develop and screen

novel libraries of products.

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