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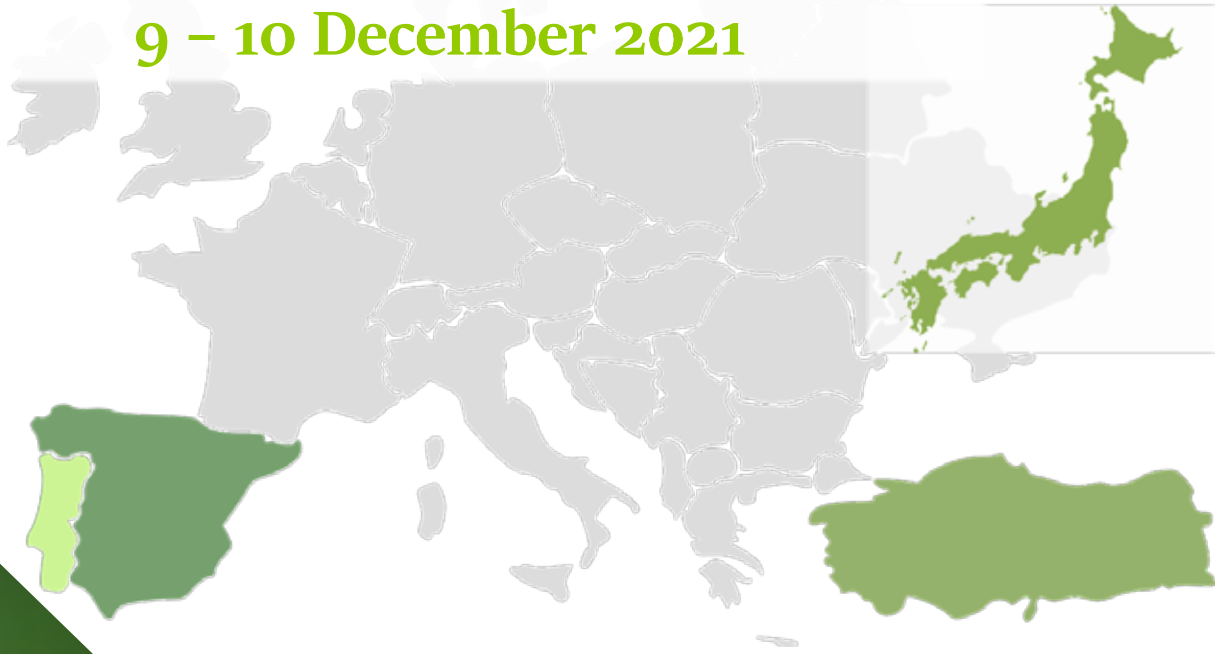

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Proceedings of the 6th International Symposium on Green and Smart Technologies for a Sustainable Society

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CONSEJO EDITORIAL

Proceedings of the 6th International Symposium on Green and Smart Technologies for a Sustainable Society

Nazely Diban, Andrea Arguillarena Maza,
Salvador Asensio Delgado,
Sergio Valentin Gutiérrez Hernández,
Raquel de la Hoz Ruiz, Marián Mantecón Oria,
Marta Romay Romero
(eds.)

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Santander, 2021

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- Raquel de la Hoz Ruiz
- Marián Mantecón Oria
- Marta Romay Romero

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Preface

Welcome to the 6th International Symposium on Green and Smart Technologies!

The 6th International Symposium on Green and Smart Technologies hosts research speakers from University of NOVA de Lisboa (Portugal), University of Zaragoza (Spain), Yamaguchi University (Japan), Atilim University (Turkey) and University of Cantabria (Spain).

This symposium, originally founded in 2013 by Universidade Nova de Lisboa, Universidad de Zaragoza and University of Yamaguchi, is conceived as an international forum for the dissemination and reinforcement of research collaboration among the participating institutions. Different institutions have been invited to participate in subsequent editions. University of Cantabria had the opportunity to participate in the 2nd and 5th edition, and we are honoured to organize the present 6th conference, that unfortunately, was forced to be celebrated remotely due to the COVID-19 global pandemic.

This edition continues with the topics discussed in the previous symposium. Scientific topics are aligned with the 2030 Agenda for Sustainable Development, and aimed at the study of key-enabling technologies and processes to ensure a sustainable industry for the society of the future.

As a novelty in this edition, the symposium will consist of 2 events that will take place in parallel:

- Live online scientific seminars given by reputed experts in the field of Chemical Engineering and related complementary scientific areas.
- Students workshop aimed at the dissemination of the research activities of PhD and MS candidates.

A special seminar session has been included, devoted to the dissemination of research goals and collaborative outcomes of the X-MEM project (5th EIG-Concert Japan joint call on “Porous structured materials”), with a partnership composed of researchers from University of Cantabria (Spain), University of Yamaguchi (Japan), Atilim University (Turkey), Ege University (Turkey), Hacettepe University (Turkey) and Jerzy Haber Institute of Catalysis and Surface Chemistry (Poland).

I hope you will enjoy the activities and that our next meeting can be celebrated face-to-face.

Nazely Diban

KEYNOTE LECTURES

Membrane Devices for Protein Crystallization

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BIOGRAPHY

Professor of Chemical Engineering at the Faculty of Sciences and Technology - Universidade Nova de Lisboa, Portugal. Director of the Laboratory of Membrane Processes at iBET, Potugal. Former Vice-Rector for Research and Innovation at NOVA and former Coordinator of NOVA Doctoral School. Former Vice-President of the Portuguese National Science Foundation. Member of “Academia de Engenharia”, Portugal. Member of the editorial board of “Journal of Membrane Science”, “Journal of Biotechnology” and “Desalination and Water Treatment”. Author of more than 310 papers in peer reviewed journals (h factor 55). Founder of the spin-off company “Zeyton Nutraceuticals”.

Membrane Devices for Protein Crystallization

Mariella Polino, Carla Portugal, Isabel Coelhoso, João Crespo

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In this work the fine control that ion-exchange membranes can provide to crystallization and derivatization of proteins has been combined with the advantages of microfluidics technology for protein crystallization (high throughput, low budget). A commercial 117 Nafion® membrane, was sandwiched between a channels' layer and a wells layer of PDMS, in order to build a microdevice with 75 micro-contactors (Figure 1) in which nano to micro volumes of protein solution can be used to control protein crystallization. Crystallization and derivatization experiments with Hen Egg White Lysozyme were performed in order to test reproducibility and the functionality of the device. The number and size of crystals were controlled by changing the volume of solution in the microdevice wells for the same area of transport through the membrane. Crystallographic analysis confirmed the high diffraction quality of crystals formed in the microdevice and the formation of stable crystal derivatives that allowed structure solution.

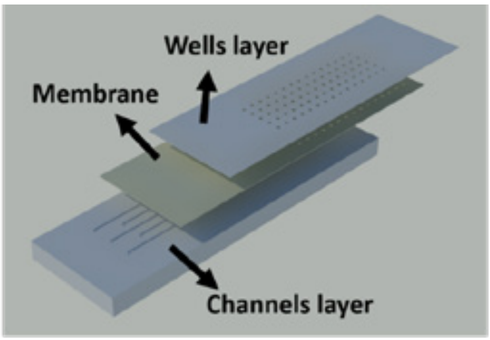

Fig. 1. Scheme of microcontactor device used for protein crystallization

Funding/acknowledgments

This research was performed in collaboration with Professors Reyes Mallada and María Pilar Pina from the University of Zaragoza, and also with Dr. Ana Luísa Carvalho and Professor Maria João Romão from UCIBIO, NOVA School of Science and Technology, Universidade NOVA de Lisboa.

Mariella Polino acknowledges the Executive Agency for Education, Audiovisual & Culture (EACEA) of the European Commission for the scholarship grant of the EUDIME programme. This research was funded by the Associate Laboratory for Green Chemistry-LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020).

Integration of membrane filtration and electrochemical oxidation for water treatment

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Professor of Chemical Engineering at the University of Cantabria, where serves as Head of the Department of Chemical and Biomolecular Engineering. She holds a degree in Industrial Chemistry, a MSc in Materials Engineering and a PhD in Chemical Engineering. Ane Urtiaga's research focuses on membrane separation and environmental electrochemistry, and their applications for improving the sustainability of the process industry, water treatment and resource recovery.Founder of the spin-off company APRIA Systems SL. Orcid: 0000-0002-8189-9171, h factor 43 (Web of Science, December 2021).

Integration of membrane filtration and electrochemical oxidation for water treatment

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The development of hybrid processes that combine electrochemical and membrane technologies is gaining importance in the area of environmental electrochemistry. Different process integration strategies will be discussed. The first approach considers electrocoagulation and electrooxidation as pretreatment of membrane separation, aimed at reducing membrane fouling and to mitigate the decay of permeate flux typically observed in porous ultrafiltration membranes. In a second approach, pressure driven nanofiltration or reverse osmosis membranes are applied to produce high quality permeate water, at the same time the retentate increases its concentration of persistent pollutants and salts. The latter conditions result in faster electrooxidation kinetics at a lower power demand of the electrochemical stage, compared to the reference case of direct electrooxidation. These properties conduct to the optimal integration of technologies using process systems engineering tools, for producing a single purified water stream, considering not only the minimization of the energy consumption but also of the total costs. Overall, process integration allows a significant reduction of the electrochemical reactor size, making the integrated process much less energy demanding that the ELOX-only approach, thus providing the desirable process intensification [1,2].

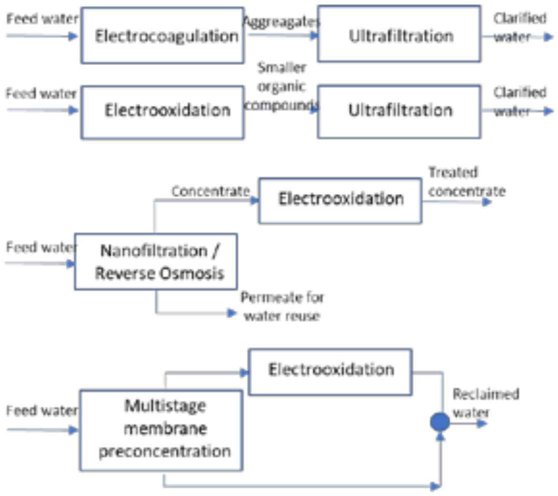

Fig. 1. Process integration strategies in environmental electrochemistry.

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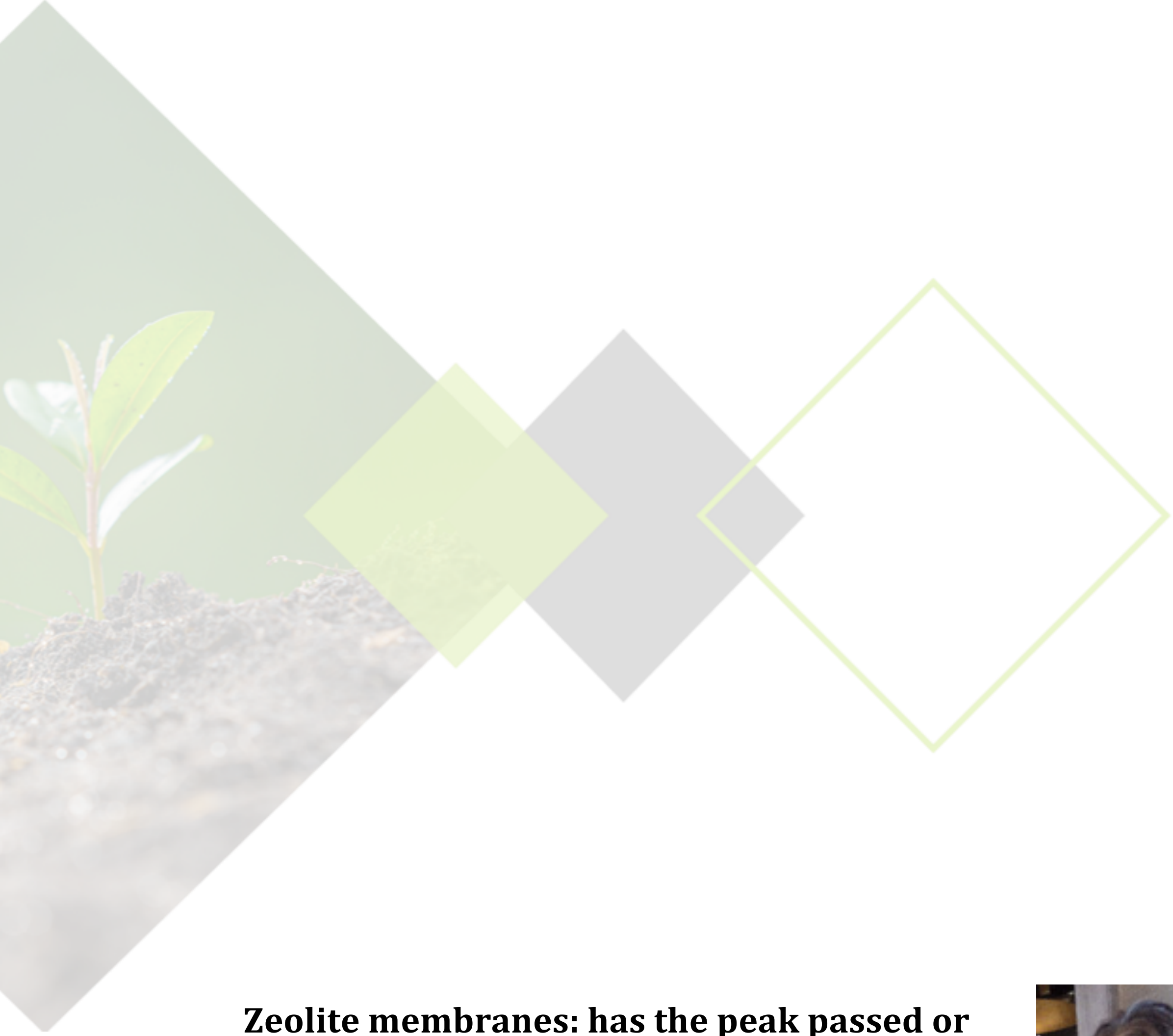

Zeolite membranes: has the peak passed or still to come?

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BIOGRAPHY

Izumi Kumakiri is currently Professor at Yamaguchi University Japan, having previously worked at National Center for Scientific Research (CNRS), France, and at Stiftelsen for industriell og teknisk forskning (SINTEF), Norway, and is involved in various national, international, and industrial projects on the developments and the applications of membranes and nano-functionalized materials. Professor Kumakiri is currently conducting research projects related to the developments of microporous inorganic membranes including carbon, zeolite, and other types, and their applications in energy and environmental fields.

“Zeolite membranes:
has the peak passed or still to come? ”

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Short abstract

Zeolites are alumino-silicate crystalline materials, having sub-nanometer ordered pores in its structure. They have been drawing a large interest as a membrane material, due to their unique adsorption ability and their pore structure having the size of molecules.

Zeolite membranes were the first micro-porous inorganic membranes commercialized. An industrial application was reported by Mitsui Ship Engineering in 1998. They scaled-up the fabrication of A-type zeolite membranes through a cooperation with Yamaguchi University, designed a module and a process, and applied the membranes to dry solvents. Since then, the number of dehydration zeolite membranes applied industrially is increasing. However, the market size is still much smaller than polymeric membranes.

One of the drawbacks of inorganic membranes, including zeolite membranes, is the high cost of the membrane. In general, zeolite membranes are formed on a porous support as a polycrystalline film. The support cost sometimes accounts more than half of the membrane cost. Reducing the membrane cost by reducing the support cost has been an important topic, but yet needs more developments.

Processes where conventional polymeric membranes or other separation technologies have difficulties to be applied are other areas to investigate the application of zeolite membranes. One of such areas is the configuration of membrane reactors. For example, there are many reactions that co-produce water and are equilibrium limited. In such case, the yield can be enhanced by removing water *in situ.* Alternatively, the nano-space in zeolites can be used as a host to disperse cluster-sized catalysts. Such zeolite composite membranes may improve the membrane reactor properties.

In this presentation, typical synthesis conditions of zeolite membranes and some examples of classic separation performance will be summarized. Then, current attemps to extend the usage of zeolite membranes will be discussed.

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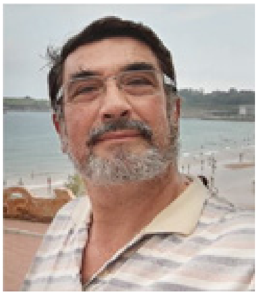
We acknowledge financial supports from Japan Science e-ASIA Joint Research Program JPMJSC16E5, JST SICORP Grant Number JPMJSC18C5, Low Carbon Technology Research and Development Program, MEXT/JSPS KAKENHI Grant Number 21K04751.

An history on zeolite membrane reactors



Prof. Miguel Menéndez
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BIOGRAPHY

Miguel Menendez is Professor of Chemical Engineering at the University of Zaragoza (Spain). His research has been devoted to catalytic reactors and membranes. In the last 30 years has been focused mainly in new catalytic reactors, including membrane reactors and two-zone fluidized bed reactors. He has published 162 articles in scientific journals, and has authored 9 patents. He has an H-index of 38 (WoK) and a Google index of 44. He has been editor of the book "Inorganic Membranes, synthesis, characterization and Applications" (Elsevier 2008). He has served as reviewer of research projects for several national research agencies and as panel member for the European Research Council (Advanced Grants-Panel PE8: Product and process engineering).

An history on zeolite membrane reactors

Miguel Menéndez

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Membrane reactors may improve the performance of a catalytic reaction by combining the actions of the catalyst and the membrane. Membrane reactors are a key instrument in process intensification. A relatively recent category among this kind are zeolite membrane reactors, which include the special type of membrane named zeolite membrane. Usually, the zeolite membrane is selective to the permeation of one of the reaction products, and the removal of this product improves the achievable yield.

This presentation will describe the history of developments on zeolite membranes at the University of Zaragoza. It will cover the origin of the idea, the successive developments and applications and the interactions with the developments from other groups that have worked in this topic [1-3].

The applications to be discussed include methanol synthesis, Fischer-Tropsch synthesis, DME synthesis, butane dimerization, esterification and ketalization.

Finally, a prospective for the future development in this field will be presented, taking into account some recent results.

Funding/acknowledgments

Current research in zeolite membrane reactors is supported by project PID2019-106196RB-I00 funded by MCIN/ AEI/10.13039/501100011033

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INVITED LECTURES

Expression of interleukin-36 family proteins in yeasts for drug development

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BIOGRAPHY

Hisashi Hoshida is Professor at the Division of Applied Chemistry, Graduate School of Sciences and Technology for Innovation, Yamaguchi University. He is currently studying heterologous protein expression and useful material production mainly using yeasts. His research work is published in the areas of Biochemistry, Genetics, Molecular Biology, Microbiology and Biotechnology.

Expression of interleukin-36 family proteins in yeasts for drug development

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Interleukin (IL) is a group of proteins for intercellular communication and plays a major role in immune system to protect our bodies from bacteria, virus and fungi. However, sometimes immune system attack our bodies themselves and causes autoimmune disorders. In general, autoimmune disorders cannot be cured and difficult to control the symptoms. Psoriasis is an autoimmune disorder. The major symptoms are red patches of skin, small scaling spots and itching. Prevalence of psoriasis in Japan is lower than 0.5%. On the other hand, those in European countries are 3-5% and many patients are suffered from the symptoms. Therefore, effective medicines and better therapies are expected to be developed. The mechanism of psoriasis is said as follows; IL-36 family proteins are involved in psoriasis. Among them, IL-36A, IL-36B, and IL36G bind to a receptor protein IL1RL2 on cell surface and activate inflammatory responses. Another IL-36 family protein, IL-36RN, also binds to the receptor. However, IL-36RN does not activate inflammatory responses and inhibit binding of the other IL-36 proteins, indicating that IL-36RN prevent strong inflammatory responses. Imbalance of these IL-36 proteins causes psoriasis. In this study, we produced IL-36 family proteins in yeasts and *Escherichia coli* as recombinant proteins to develop medicines against psoriasis. In addition, we developed a yeast-based system to analyze binding of IL-36 proteins and the receptor protein. For production of recombinant IL-36 proteins, the yeasts *Saccharomyces cerevisiae* and *Kluyveromyces lactice* were used. The yeasts have own high-copy plasmids. Recently we developed expression plasmids based on the native plasmids of the yeasts. IL-36 genes were cloned into the plasmids and expressed in *S. cerevisiae* and *K. lactice*. The yeast cells were cultured, and proteins were extracted and production levels were analyzed by SDS-PAGE. As a result, a strong band of IL-36B protein and a band of IL-36G protein were detected. However, IL-36A was hardly produced and IL-36RN were not detected. These genes were also cloned into an expression plasmid in *E. coli*. The production levels of the IL-36 proteins in *E. coli* were similar with those in the yeasts, suggesting that expression levels may depend on protein structures but not intracellular environment and expression systems of host cells. To develop IL-36 protein variants which are suitable as medicine to cure psoriasis, an effective and convenient system to analyze binding of variant proteins and the receptor protein is required. For this purpose, we expressed IL-36RN and IL1RL2 in the cell of *S. cerevisiae*. To detect binding of the proteins, these proteins were fused with fluorescent proteins and the cells were observed with a fluorescent microcopy. When IL1RL2 was expressed as a fusion protein with a green fluorescent protein (GFP), green dots were observed in the cells. On the other hand, IL-36RN fused with a red fluorescent protein (RFP) dispersed in cytosol. When these fusion proteins were expressed simultaneously in the cells, RFP fluorescent showed week dots at the same position with GFP dots, suggesting that IL-36RN binds to IL1RL2 receptor in the cells. We also found that several IL-36RN mutations enhanced dot formation in the cells expressing the receptor protein. These results indicated that this binding assay system will be helpful to develop IL-36 variants suitable for psoriasis treatment.

Nanostructured materials and membranes

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Reyes Mallada currently works at the Department of Chemical Engineering and Environmental Technology, University of Zaragoza. Her research interests are in Chemical Engineering, Materials Chemistry, Membranes, Catalysis and Microwave driven synthesis and catalysis. Reyes Mallada has published, a total of 110 publications in peer reviewed journals in specialized fields such as membranes i.e. Journal of Membrane Science (11), catalysis in Applied Catalysis A (6) and B (1), Catal Today (8), J Catal (1) and in journals devoted to Chemical Engineering i.e. Chem. Eng J (6) and Ind. Eng. Chem. Res (4). In the last years, she has published in high impact factor journals such as Applied Materials and Interfaces, Science Advances and Angewandte Chemie. Many of these publications are in collaboration with other international groups in different countries, Netherlands, France, Portugal, Argentina, Germany, Denmark, etc.

Nanostructured materials and membranes

Reyes Mallada

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Nanostructured materials are defined as those exhibiting at least one of its dimensions below 100nm. The key factor is that as soon as the size of the materials goes down to the nanoscale, new fascinating properties emerged. One of the first approaches consisted of the incorporation of porous nanomaterials into the membrane giving rise to the so called mixed-matrix membranes, with enhanced selectivity and flux in gas separation membranes. The participation of the Institute of Nanoscience of Aragon in the Erasmus Mundus Doctorate and Master programs, in a fruitful collaboration with leading experts' universities in the field of membranes, U. Nova de Lisboa, U.de Montpellier, U. de Calabria and U. of Twente, have resulted in co-supervised PhD and Master thesis incorporating nanostructured materials. The goal was to exploit the new properties achieved in the nanoscale for solving or understanding common problems faced in the field of membrane technology.

In this sense we will discussed three different examples, i) The synthesis of membranes based on self-assembled block copolymer nanoparticles together with magnetic nanoparticles resulted in membranes with define nanopore architecture, responsive to magnetic flied that have been used for ultrafiltration of proteins. Tunning the magnetic field is possible to partially control membrane fouling [1,2]. ii) The incorporation of thermoresponsive nanoparticles on the surface of membranes made possible to directly monitor the temperature on the surface on the membrane instead of on the bulk liquid during membrane distillation process, understanding thermal polarization phenomena [3,4] iii) Protein membrane crystallization is affected by the transport of ions through the membrane, but also by the hydrophobic or hydrophilic properties of the surface. In this case the approach included the micro and nanostructuration, by nanoimprint lithography (NIL), of the surface of ion-exchanged membrane (Nafion) followed by its incorporation in a microfluidic chamber [5,6].

Funding/acknowledgments

This work has been financed by the Education, Audiovisual and Culture Executive Agency (EACEA) under the Program "Erasmus Mundus Doctorate in Membrane Engineering"–EUDIME (FPA 2011–2014, http://www.eudime.unical.it).

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Integration of magnetic nanomaterials and microfluidics for targeted separation of biomolecules

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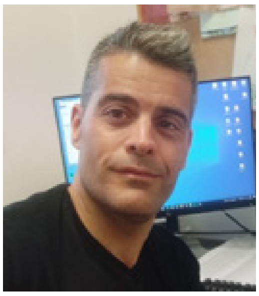

BIOGRAPHY

Eugenio Bringas is Associate Professor of Chemical Engineering at the University of Cantabria (Spain). His research has been focused on the design of advanced separation processes and on the use of magnetic materials on separation applications. Since 2003, he has published 49 articles in scientific journals and participated in more than 20 national and international research projects. He has an H-index of 18 (Scopus). He has contributed to more than 70 international conference and supervised 5 PhD thesis.

Integration of magnetic nanomaterials and microfluidics for targeted separation of biomolecules

Eugenio Bringas

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Research on magnetic nanoparticles (MNPs) is currently an area of intense scientific interest in a wide variety of technological areas, due to the great potential of these materials. In general, MNPs exhibit enhanced physical and chemical properties, i.e. superparamagnetism, chemical reactivity, surface area, as compared to macroscopic materials and thus, their integration in existing technologies could lead to energetically and economically more efficient processes [1].

Separation of highly valuable or toxic compounds from biological fluids using MNPs is receiving increasing attention since they provide outstanding properties which allow to overcome the drawbacks of existing applications [2]. The recent advances in synthesis methods enable the coating of different functional groups on the surface of the MNPs, which work as specific binding sites, increasing the adsorption capacity and improving the selectivity of the process. Finally, due to the small size of these nanocomposites (which can vary from tens to hundreds of nanometers) and the fact that MNPs are superparamagnetic, the use of magnet-based separation provides a very simple and effective method of recovering these particles from the solution.

The integration of the magnetic particle separation stage into continuous microfluidic devices leads to the development of microfluidic-magnetophoretic separation devices, which make use of the inherent advantages of microfluidics. One of them is the laminar flow profile developed by the fluids inside the microdevices that theoretically allows to maintain unchanged the flow patterns. Thus, continuous devices employing different fluid phases, i.e. the treated biological fluid with the MNPs and a buffer solution which would act as a collecting fluid, could be employed for the MNPs separation when an external magnetic field is applied as depicted in Figure 1.

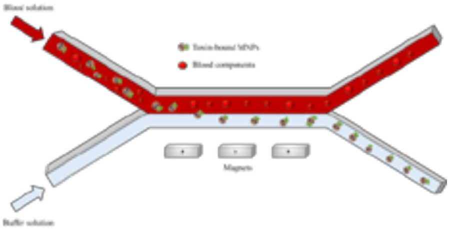

Fig. 1. Scheme of microcontactor device used for protein crystallization

This work provides the guidelines to design magnetophoretic microfluidic systems to be employed in the separation of targeted biomolecules. In particular, the removal endotoxins from blood in sepsis therapy is selected as case study.

Funding/Acknowledgements

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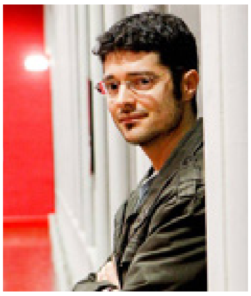
Production of hybrid nanomaterials: case studies and applications



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Dr. Victor Sebastian Cabeza, is Associate professor at the Chemical Engineering Department-University of Zaragoza and senior researcher at the Nanoscience & Materials Institute of Aragon (Spain). Dr. Sebastian is leading an innovative research in the field of nanomaterials engineering using microfluidics as a platform to control the reaction conditions to tune the wide range of properties of nanomaterials. He is coauthor of 210 publication, 2 patents, 6 book chapters, h index= 38 with more than 4700 cites -SCOPUS (ORCID iD = 0000-0002-6873-5244).

Production of hybrid nanomaterials: case studies and applications

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The combination of biopolymers and metal nanoparticles (NPs) as hybrid nanostructures can perform several functions other than drug delivery, emerging as promising combination vectors in the new class of theragnostics used in highly sensitive biodetection, [1] medical imaging [2] and triggered drug delivery [3]. Metal NPs can be either incorporated into the inner NP space or attached on the surface of the nanoentity. This type of hybrid NPs are usually produced by complex multi-stage procedures based on the covalent and non-covalent grafting to polymers of preformed metal NPs. Although some of the reported procedures based on those previous strategies are easy to implement, the loading control of metal NPs is poor and its reproducibility limited. Our group developed a novel procedure to circumvent the weaknesses of some of the previous production techniques [4]. This procedure was based on the in-situ reduction of metal ions loaded in the internal aqueous phase of a water-oil-water (w/o/w) polymeric double-emulsion of PLGA. After the emulsification process, the ions were reduced on demand by the citrate ions present in the emulsion using a redox process activated by temperature at soft conditions (40°C) to preserve the polymer properties. Following this procedure, a tunable payload of spherical Au NPs (size ≈ 10 nm) could be encapsulated in each PLGA NP (size ≈ 175 nm) [4]. A further development was carried out by developing a continuous, robust and scalable process to prepare these hybrid metal-polymeric NPs by a microchannel emulsification process [5]. In this case a three-stage process in continuous flow was designed; the first two stages were aimed at the production of the w/o/w PLGA double-emulsion and the loading of the reducing agent, as well as the Au precursor. Finally, the third stage was devoted to supply for 10 minutes the thermal energy required to activate the redox process. This procedure was able to supply a continuous production of Au-loaded PLGA hybrid NPs of 2.8 mg/s [5].

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Multicomponent iongel membranes for CO_2 separation applications

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Multicomponent iongel membranes for CO_2 separation applications

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Due to their remarkable CO_2 affinity, as well as tuneable nature, there has been a growing interest in the exploitation of IL-based materials for CO_2 separation membranes [1]. In this context, the development of iongel membranes, with a high IL content (>60 wt%) is a promising strategy to obtain high gas separation performances, while at the same time overcome the stability issues reported for supported IL membranes or the limitations in the polymer/IL composition of poly(ionic liquid)-based membranes.

In this communication, two and three-component iongel membranes consisted of a cross-linked polymer network (PEGDA), ionic liquids (ILs), and azo-linked porous organic polymers (azo-POPs) will be presented [2-3]. The membranes were prepared by UV-initiated free radical polymerization. The obtained cross-linked iongel membranes were characterized in terms of structural, thermal, mechanical and morphological properties. Gas permeation experiments were also performed and the results were compared to the Robeson’s upper bound limits.

The aim is to show the versatility of these materials, point up their easy preparation, and reveal insights into the relationships between gas transport properties, IL structures, diverse azo-POPs and iongel compositions. Breakthroughs and key challenges will be discussed, as well as possible paths for future research.

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Synthetic Natural Gas by biogas upgrading: catalysts, reactors and process configurations

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Synthetic Natural Gas by biogas upgrading: catalysts, reactors and process configurations

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Shortage of fossil fuels coupled with the progressive global heating caused by GHG are forcing the mankind to search for new methods for obtaining energy. These should be based in renewable sources and must minimize wastes. An interesting candidate for supplying this “clean” energy is the electricity based in sun or wind. The key issue concerning these sources is that they are fluctuating and not predictable in the long term. Production of synthetic natural gas (SNG) appears as a viable proposal storing energy in “valley” periods (low demand), producing electrolytic hydrogen that can be easily stored. On the other hand, biogas is the product obtained from the anaerobic decomposition of organic matter. It contains significant proportions of carbon dioxide and methane. It is produced from MSW, solids from WWTP, digestion of manure or other industrial residues. Hydrogen can react with carbon dioxide present in the biogas producing methane that can be injected in the current natural gas distribution net. On this way, upgraded biogas [1] can be converted both in an energy reservoir and an energy vector easily distributed without investing more capitals devoted to logistics of distribution.

Several catalysts and alternative reactor configurations have been tested in our laboratory. Among them, catalyst with a dual function (DFM), performing the Sabatier reaction (methanation) while adsorbing water [2], pushing the thermodynamic equilibria beyond its natural limits, are showing very promising results.

Funding/acknowledgments

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Sustainable production of hydrophobic deep eutectic solvents based-nanoemulsions by membrane emulsification for biomedical applications

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Sustainable production of hydrophobic deep eutectic solvents based-nanoemulsions by membrane emulsification for biomedical applications

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In the quest for replacing toxic, volatile and harsh solvents, and to follow the principles of green and sustainable chemistry and engineering, various functional solvents have been proposed in the last two decades. Hydrophobic deep eutectic solvents (DESs) are a recent class of designer green solvents substituting ionic liquids as they offer low cost and negligible toxicity [1]. Currently, these are exploited for extraction and environmental purposes. However, in order to potentiate bio-based applications wherein polar media is usually encountered, the low solubility of these hydrophobic solvents in water was addressed in this work by dispersing them as nanoemulsions [2].

Membrane emulsification was introduced in the end of the last century as an energy-efficient method to produce microemulsions. In the current study, hydrophobic DES-in-water nanoemulsions were sustainably produced by membrane emulsification. Firstly, various terpenes-based hydrophobic DES were synthesised from therapeutic compounds such as menthol, thymol and decanoic acid. Parallelly, microengineered isoporous membranes (9 µm pore size) with controlled geometry were fabricated by low energy-intensive and solvent-free laser machining technique. Under optimised operating conditions, menthol/decanoic acid-based and menthol/thymol-based hydrophobic DES-in-water nanoemulsions (58.7±0.4 nm and 81.2±0.9 nm respectively) were sustainably produced by membrane emulsification. The intrinsic quality of hydrophobic DES to self-assemble into monomodal narrow size distribution of nano-droplets while using a 9 µm isoporous membrane led to a new phenomenon termed as membrane assisted nanoemulsification process.

From the application perspective, the optimised DES-based nanoemulsions were subjected to antimicrobial susceptibility testing assays. In contrast to the non-emulsified DES or its individual components (menthol and decanoic acid), 16 times less chemicals were required when tested as nanoemulsions to inhibit bacterial activity of *S. aureus* and *E. coli*[2]. This suggests increased bioavailability and a synergistic effect of all components in nanoemulsions potentiating their antibacterial activity. Moreover, menthol/thymol based hydrophobic DES-in-water nanoemulsions exhibited increased antibacterial activities and were also highly effective against *C. acnes*, an acnes inducing bacteria.
Lastly, membrane-assisted nanoemulsification offers sustainable production of nanoemulsions with a better control over size and dispersity along with lowered energy consumption when compared to conventional emulsification techniques.

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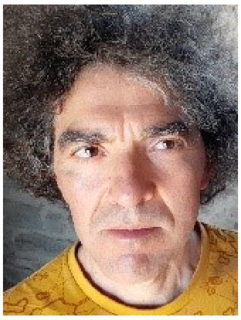

Green method to obtain thin film composite membranes for nanofiltration

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Green method to obtain thin film composite membranes for nanofiltration

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Thin film composite membranes (TFC) of polyamide (PA) prepared by interfacial polymerization (IP) between a diamine and an acyl chloride are those applied to industrial nanofiltration and reverse osmosis. Water, to dissolve the diamine, and n-hexane, to dissolve the acyl chloride, solvents are involved in the IP process. Eliminating the use of n-hexane would be crucial to produce a greener TFC membrane synthesis method. This is achieved here by carrying out an interfacial polymerization from the vapor phase. First, the membrane support was impregnated with the aqueous diamine solution. Second, the support with the diamine was contacted with vapor of the acyl chloride to unchain the IP reaction. Besides the absence of n-hexane, the acyl chloride was applied more efficiently avoiding its lost during the cleaning operations carried out in the typical IP process. The membranes were applied to the nanofiltration of simulated micropollutants in water (rose Bengal, sunset yellow and acridine orange), with higher water permeance (up to 3.3 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) than that of conventional TFC membranes and rejections higher than 94 % in all cases [1].

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Monitoring of membrane processes with fluorescence techniques and machine learning approaches

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Monitoring of membrane processes with fluorescence techniques and machine learning approaches

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When monitoring complex systems, such as membrane processes (involving membrane fouling), it is essential to capture as much information as possible about the system and simultaneously process that information to assess the system status and performance in real-time. Such integration between data acquisition and data analysis will allow process monitoring and control.

The use of fluorescence spectroscopy in a broad range of excitation and emission wavelengths to assess natural fluorophores present in liquid streams and in membrane surfaces, results in large data sets (EEMs: excitation-emission matrices) that can be seen as fingerprints of system status. However, in such complex data sets, direct interpretation of data is prevented due to the presence of several fluorophores and interfering effects (caused by fluorescent and non-fluorescent compounds). Thus, artificial intelligence and machine learning approaches can be used to analyze and extract useful information from fluorescence EEMs. The development of mathematical models is essential to correlate the experimental measurements with relevant operating or performance process parameters, fouling potential and fouling evolution/prediction and is also required for the development of effective control tools.

This approach was successfully applied to monitor process performance in membrane bioreactors [1] and cell integrity during ultrafiltration of microalgae [2], which are both highly complex systems due to the presence of microorganisms and of biological products. Furthermore, it was also used to assess membrane surfaces during a reverse electrodialysis (RED) process [3], to follow the development of fouling and characterize the effects of fouling and of membrane cleaning efficiency, allowing for membrane surface characterization and monitoring of the membrane status. More recently, this approach was applied to characterize and compare the surface of modified membranes used for nitrate removal by Donnan dialysis and anion-exchange membrane bioreactor, revealing different degrees of alterations induced by fouling and chemical cleaning.

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Atomistic Study of CO_2-selective Mixed Matrix Membranes. Describing the role of the ionic liquid

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Atomistic Study of CO_2-selective Mixed Matrix Membranes. Describing the role of the ionic liquid

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The capture of the greenhouse gas CO_2 has become one of the main challenges of this century due to environmental adverse effects. Among the emerging technologies, this work focuses on the preparation and characterization of CO_2 selective mixed matrix membranes (MMMs) composed by Metal-Organic Frameworks (MOFs) and Ionic Liquids (ILs) into a polymeric matrix.

However, as consequence of their limitless combinations, this work aims to provide a hybrid comprehensive analysis of experimental data and molecular dynamics simulations to determine the key factors in IL-ZIF-8-MMMs preparation for CO_2 separation performance. The main factors addressed in this study include IL structure, IL/ZIF-8 concentration and, IL/ZIF-8 location in the MMM (Figure 1).

The optimal material arrangements for selective CO_2 separation were successfully modeled and were found to be strongly dependent on the IL loading. It is also described the potential of this methodology to have membrane preparation guidelines, potentially to be extended to other novel materials.

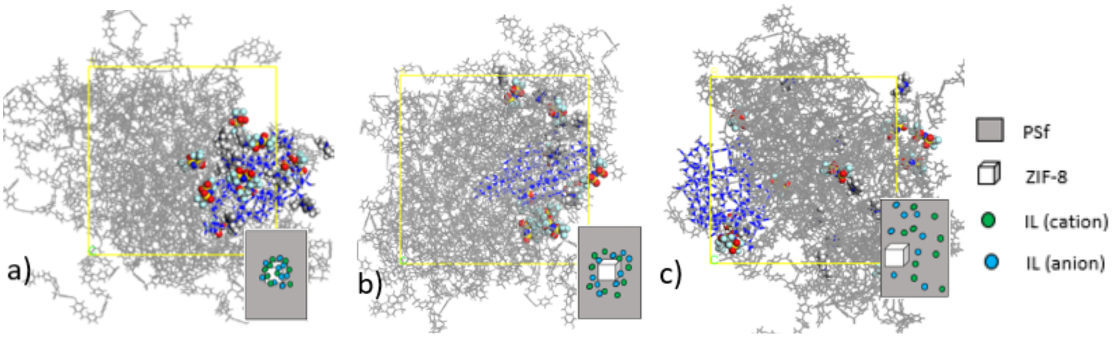

Fig. 1. MMMs modeled configurations with schematic description for: a) incorporation of IL inside of ZIF-8; b) external coverage of ZIF-8 with IL; and c) free dispersion of ZIF-8 and IL.

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Why photocatalysis can be considered as a Green Technology for a Sustainable Development?

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Dr. Maria J. Rivero is Associate Professor since 2012 and carries out her activity in the Department of Chemical and Biomolecular Engineering of the University of Cantabria. Trained as an Industrial Engineer in the specialty of Industrial Chemistry, she obtained a Doctorate from the University of Cantabria in 2002. Most of her research has been focused on the treatment of aqueous streams. She began working on membrane separation processes, ion exchange and adsorption; to continue with Advanced Oxidation Processes (AOPs) such as Fenton, photo-Fenton, electrochemical oxidation, and photocatalysis. After a 6-month postdoctoral stay at Cranfield University (United Kingdom) she has dedicated much of her research to improve the design of photocatalytic reactors with the aim of optimizing the energy efficiency, for example through the use of new systems of LED lighting. In this same field of expertise, she is currently working on the design of new catalysts. Some of them based on particles with magnetic properties that facilitates their separation and subsequent reuse. Other type of particles are synthesized with graphene oxide, which is intended to improve properties of the catalyst and modify its bandgap so that they can be activated in the presence of solar radiation. The third type of catalysts studied includes metals so that the plasmonic effect improves photocatalytic results. Some of the new materials have been also used for the photocatalytic generation of hydrogen.

Why Photocatalysis can be Considered as a Green Technology for a Sustainable Development?

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In photocatalysis a chemical reaction is initiated with the absorption of light by a catalyst. When light comes from the sun it can be considered as a green and sustainable technology. Depending on whether the catalyst is solid or in solution, it can be homogeneous or heterogeneous. In the case of heterogeneous photocatalysis, semiconductor materials such as titanium dioxide can be used as catalyst. When the material is illuminated with the appropriate wavelength, an electron from the valence band can move to the conduction band (Fig. 1). In aqueous phase and with the presence of oxygen, hydroxyl and superoxide radicals are formed. Both of them can attack organic molecules leading to their destruction. Therefore, this technology can be used to remove organic contaminants from water such as pesticides, pharmaceutical compounds, surfactants, or microorganisms and viruses to get clean and safe water in the frame of sustainable development goal (SDG) number 6 (Clean water and sanitation) [1].

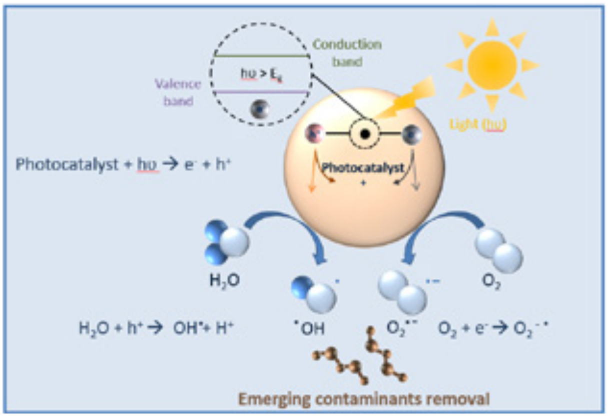

Fig. 1. Photocatalysis scheme

When there is no oxygen, this mechanism can lead to hydrogen generation [2]. This will be considered within the scope of SDG number 7 (Affordable and clean energy) and goal 13 (Climate action).

Nevertheless, several issues remain still challenging for process scale-up and industrial implementation worldwide, such as i) availability of photocatalytic materials with high effectiveness under visible light irradiation and low recombination of electron-hole pairs, ii) catalyst recovery and reusability or iii) optimized reactor design and engineering.

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Porous polymer membranes functionalized with active materials for societal challenges

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Porous polymer membranes functionalized with active materials for societal challenges

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The X-MEM consortium aims at developing new and functionally ameliorated porous membrane materials contributing to have ‘Clean water’, ‘Green Energy’ and ‘Good Health’.

Membrane porous structure is crucial on the one hand in terms of transport properties; and on the other hand, by increasing/facilitating surface contact area with the active materials potentially immobilized in the membrane matrix [1].

The consortium partners are involved in several inter-collaborative activities, that in the context of ‘Clean Water’ and ‘Good Health’, include:

i) Development of new active materials, or screening of existent ones, seeking for improved functionality [2].
ii) Modelling variables influence on polymer membranes porosity for the typical synthesis technique of solvent induced phase separation [3].
iii) Membranes characterization and assessment of performance of the membranes containing the active materials [4].

In this presentation the main objectives, strategies and outcomes of the project focused on the ‘Clean Water’ and ‘Good Health’ societal challenges will be introduced.

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Ion exchange membranes with enhanced antifouling properties to produce energy from renewable sources

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BIOGRAPHY

Enver Güler is currently assistant professor at Chemical Engineering in Atilim University, Ankara, Turkey. He was post-doctoral researcher at Sabanci University Nanotechnology Research and Application Center (SUNUM), Istanbul, from 2015 to 2017. In addition, he worked as researcher at Wetsus - water technology institute in Leeuwarden, the Netherlands in 2014. He received both bachelor (BSc) and master (MSc) diploma in chemical engineering, in 2007 and 2009, respectively, from Ege University in Izmir, Turkey. Later, he received his PhD in chemical engineering from University of Twente, the Netherlands in 2013. From 2009-2013, he worked in Membrane Science and Technology Group (MST) in University of Twente for his PhD studies. For a year during that period (2012-2013), he worked full-time as visiting researcher at FujiFilm company (Tilburg) in the Netherlands. With an h-index of 14, he is the author or co-author of 25 scientific papers published in highly rated peer-reviewed journals such as Journal of Membrane Science and ChemSusChem. He is also a co-author of two book chapters published in 2016 via CRC press and in 2018 via Elsevier. As a reviewer, he functions in more than 15 scholarly journals, had several reviewer recognitions. He is recipient of the outstanding `Best PhD Paper of the Year 2014 Award` from Twente Water Center in University of Twente. He received Best Poster Prize in IEX 2008 conference held in University of Cambridge in UK. Up to now, he contributed to 4 national and 3 international projects. His main interests are membrane synthesis, membrane separation processes, salinity gradient energy and polymer electrolyte fuel cells.

Ion exchange membranes with enhanced antifouling properties to produce energy from renewable sources

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The X-MEM consortium aims at developing new and functionally ameliorated porous membrane materials contributing to have ‘Clean water’, ‘Green Energy’ and ‘Good Health’. The X-MEM project aims at gaining insights on functionality in terms of reactivity, selectivity and efficiency of photocatalytic- and electro-active porous materials using systematization of synthesis variables and nano-scale management approaches.

In the context of ‘Green Energy’, we particularly apply this methodology to develop and improve the functionality of anion exchange membranes (AEMs) with porous substrate to be used in reverse electrodialysis (RED) to generate salinity gradient power. AEMs are more prone to fouling and usually more complex to synthesize compared to their cation exchange counterparts. Thus, novel pore filling membranes have been prepared using solvent evaporation method and tested in lab-scale RED system [1,2]. Silver nanoparticles (size ca. 100 nm) with antifouling property were integrated onto the surface of polyepichlorohydrin based anion exchange membranes by dipcoating technique [3]. To prepare thin pore filling membranes, thin commercial nonwoven substrate (ca. 160 µm) was used [4]. Membrane characterization by swelling degree, thickness, and ion exchange capacity was performed. Prepared membranes exhibited satisfying physicochemical properties providing promising RED performance.

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ABSTRACTS

(PhD WORKSHOP)

The environmental benefits of zinc and iron recovery from spent pickling acids

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Spent pickling acid (SPA) is the most abundant waste of the hot-dip galvanizing (HDG) process [1]. SPA is conventionally managed by neutralisation/precipitation (N/P), solidification/stabilisation (S/S), and landfilling. This reference practice implies the production of metallic sludges, that once in the landfill may become a source of heavy metals pollution in groundwater. In addition, N/P and S/S treatments do not allow to recover the metal resources of SPA. The project LIFE2ACID aims to promote the circular economy of HDG, recovering secondary zinc and ferrous chloride ($FeCl_2$) by means of non-dispersive solvent extraction (NDSX) and electrowinning (EW) [2].

This work aims to compare the environmental impacts of NDSX/EW with the reference treatment using the LCA methodology according to the ISO 14040 requirements. The inventory is based on pilot scale results, using one m^3 of SPA as functional unit, and CML 2001 as impact assessment method.

Fig. 1 compares the environmental impacts of waste SPA management alternatives, showing that NDSX/EW has a lower impact than the conventional treatment in all categories. In terms of energy consumption, NDSX/EW technology reduces ADP-fossil and GWP by 26% and 97% compared to conventional treatment. Toxicity is also reduced because the secondary iron and zinc products replace primary materials with the benefit of reducing the emissions of heavy metals associated to their production. Secondary zinc is a viable product in the market, and the recovered $FeCl_2$ could replace iron (III) chloride used as hydrogen sulphide suppressor in the anaerobic digestion of wastewater treatment sludge. The current context of increasing demand for metals such as zinc and the depletion of their natural reserves encourages such secondary metal alternatives. In addition, waste is transformed into secondary products, thus reducing the depletion of raw materials with a high environmental impact due to their material and energy requirements.

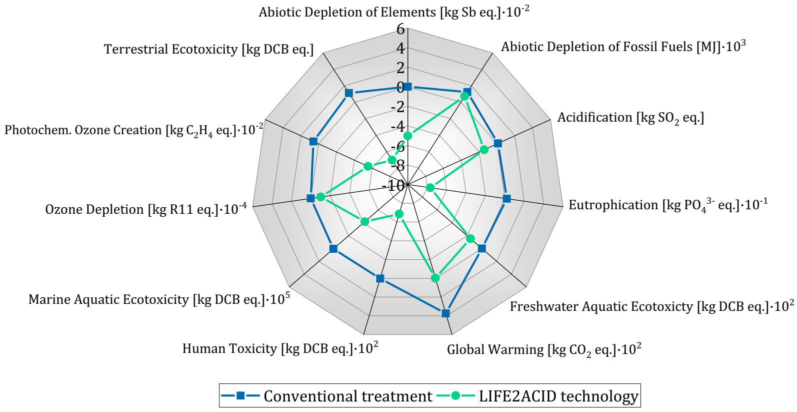

Fig. 1. Environmental impacts of SPA conventional treatment and LIFE2ACID technology per m^3 of SPA.

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Toward the development of functionalized materials for membrane separation of F-gas refrigerant mixtures

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The high global warming potential (GWP) of hydrofluorocarbons (HFCs), and the entry into force of new European (European Regulation no. 517/2014) and international regulations (Kigali amendment to Montreal Protocol), have forced the refrigeration and air conditioning (RAC) sector to look for gas refrigerant alternatives to adopt more sustainable models that allow the recovery, recycling and reuse of these gases (Circular Economy). In this regard, the RAC sector must make a transition from the use of high-GWP refrigerants, such as the R410A (HFC/HFC) mixture, to the new HFC/HFO (hydrofluoroolefin) mixtures with low GWP. Due to the near-azeotropic behavior of the R410A mixture, it is necessary to implement advanced separation processes that allow the selective separation and recovery of the high value-added HFC-R32 to be reused in the formulation of novel environmentally-friendly refrigerants.

In this work, new functionalized materials are assessed in the form of the so-called Mixed Matrix Membranes (MMMs), in order to boost the separation performance of neat rubbery polymer membranes [1,2]. In this regard, zeolite 4A has been introduced as a disperse phase within the Pebax1657® polymer matrix. The results show that the addition of zeolite 4A particles, up to 50 wt% in the hybrid material, provided a significant improvement in the gas permeability, which increased from 132 to 410 barrer. The effect of increasing the feed gas pressure and temperature had positive effect in the permeability of both gases. Moreover, the ideal gas selectivity of this MMM for the separation of R32 and R125 remained nearly constant at increasing pressures, a clear advantage in comparison with the pure polymer membrane. Furthermore, sorption experiments revealed that a MMM with a 50 wt% zeolite 4A had higher R32 sorption capacity than that of neat Pebax 1657® membranes, whereas the solubility of R125 was severely hindered. This fact is attributed to the kinetic diameter of R32 (4.02 Å), much smaller than that of R125 (4.80 Å), which makes the narrow pores of zeolite 4A (3.8 Å) more easily accessible to the R32. Overall, considering both the permeation and sorption experiments, the results suggest that the presence of interfacial non-selective voids between the zeolite particles and the polymer matrix could be limiting the enhancement of the separation factor. Further studies, will focus on the functionalization of composite membrane materials to improve the separation performance, that maintain the high R32 permeability already achieved but with enlarged separation factors.

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Towards a sustainable tourism and circular economy: Analysis of a new impact assessment model for the tourism sector

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Tourism is one of the most important sectors in the world and it is growing increasingly. However, at the same time, the CO_2 emissions associated with this activity are also growing. According to the World Tourism Organisation (UNWTO), the COVID-19 pandemic has served as a turning point for tourism activity, as during the health crisis, which was the worst shock to international tourism due to mobility restrictions, carbon emissions were reduced by 7% [1]. In this way, it is necessary to create a new tourism management system that links the circular economy with sustainable tourism, as there is a current need for innovation in the tourism sector. Hence, it will be developed a tool capable of assessing the impacts associated with each of the stages of the sector and the four sub-sectors (accommodation, catering, transport and leisure activities) and an eco-labelling system with a life cycle perspective. This work focuses on the development of a new model in the SUDOE area and it is based on Life Cycle Impact Assesment (LCA), which is one of the most promising methodologies for the analysis of the impacts of tourism activity due to its great advantages over other methods, such as carbon footprint (CF) [2].

Firstly, the boundaries of the system and the corresponding functional units (FU) for each sub-sector were defined. Then, an inventory has been performed according to the ISO 14040:2006 standard, which considers the inputs and outputs of the flows in each sub-sector. This inventory was carried out by means of web questionnaires to the different establishments. Also, the different emission factors (EF) of each study compound have been obtained from the Simapro software and the Ecoinvent database. Furthermore, this model stands out for going beyond the calculation of the (CF), as not only the category of global warming has been considered but also a wider group of 9 environmental indicators, such as Acidification, Photochemical Oxidation, Ozone Layer Depletion, Particulate Matter, Eutrophication of fresh and sea water, water use and energy. All these impact categories have been assessed according to the Product Environmental Footprint (PEF) method and the UNE-EN 15804:2012+A2:2020 standard on Sustainability in Building. The results are finally presented using a radar graph or "spider" diagram showing a comparison between the average impact of the sub-sectors in the SUDOE sub-sector area and the average impact of the sub-sectors in the destination sub-sector. In addition, as sustainable tourism has a prominent place in the 2030 Agenda, it should be linked to the Sustainable Development Goals (SDGs), specifically, with SDGs 3, 6 and 12 that are strongly related to the sector. In short, this new tool aims to become a lever for change towards the recovery of the tourism sector, which in recent months has been severely damaged by the effects of COVID-19 from a socio-economic perspective, but advantageous from an environmental point of view. On the other hand, the tourism sector will benefit from an environmental eco-label, which will allow it to enter green markets, which is an economic opportunity and will also be profitable for the public administration, which will have a validated model of sustainable tourism.

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Quantifying the sustainability of potato chips from a water-energy-food nexus approach

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Understanding sustainability and environmental impacts of agri-food supply chains has become an important issue to achieve the transition to a more efficient and resilient food sector. Agriculture activities consume vast number of resources; the cultivation, harvesting, processing and transportation of food require significant amount of electricity, crops, and water, evidencing the inextricably interconnectedness of these three sectors, constituting the water-energy-food (WEF) nexus. Potato, which is one of the most popular edible plants in the world, represents an important economic income for producing regions, mainly through its processed products, such as potato chips. However, this area of the food sector and its environmental impacts remains unexplored. Hence, this study examines the environmental sustainability issues in the water-energy-food nexus by considering potato chips manufactured by a Cantabrian industry (Spain). For this purpose, the joint application of life cycle assessment (LCA) for water (WF), energy (EF) and carbon (CF) footprints calculations, and the nutrient rich food 9.3 (NRF9.3) indicator was proposed, seeking to understand the complex interlinkages that blind WEF pillars, and to identify the main hotspots of the system, enabling to propose technical improvements and contribute to political decision-making processes. Within a life cycle thinking, a functional unit (FU) of 50 g bag of potato chips was defined, as well as a cradle-to-grave approach.

The results indicated that average greenhouse gas (GHG) emissions reach 119 g CO_2-eq. per bag, mainly generated in cultivation (45%) and processing (48%). The WF reported a water use of 1.72 m^3 per FU, with more than 90% consumed in the potato cultivation. On the contrary, the eutrophication potential, both of freshwater and marine, extended non-significative burdens, $2.15 \cdot 10^{-5}$ kg P eq./bag and $5.15 \cdot 10^{-4}$ kg N eq./ bag, respectively. Finally, energy consumption was estimated 1.45 MJ/bag, with major hotspots located in the cultivation (48%) and processing (38%) phases. Regarding nutritional aspects, a NRF9.3considering a weight basis of 72.25 was calculated, which describes a rather low nutritional value of the product, mainly due to the high amount saturated fats. Improvement actions and strategies explored in this study are focused on the cultivation and processing stages, and covered better agricultural practices, such as the application of drip irrigation or organic fertilizers, and improved energy efficiency as well as alternative renewable sources.

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ANN for GC identification of mixtures with marked matrix effect: application to SNG production

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Power-to-Gas (PtG) technologies are being under study as suitable techniques for GHG emissions reduction as well as for energy storage. Hydrogen obtained from water electrolysis and carbon dioxide of renewable origin, can be transformed into e-fuels through a methanation process leaded by the Sabatier reaction.

Complex mixtures of hydrogen, methane, carbon oxides (CO and CO_2) and inert gases (Ar and N_2), as those used in research for e-fuels production, can exhibit an unusual response when their concentration, found in a wide range, must be determined by µGC. In these cases, chromatographic peaks are heavily influenced by the concentration of each other components due to a matrix effect. This atypical behaviour, added to an observed non-linear response between concentration and chromatographic area for the quantifiable species, can lead to serious misinterpretations of the performance of the catalytic reactor.

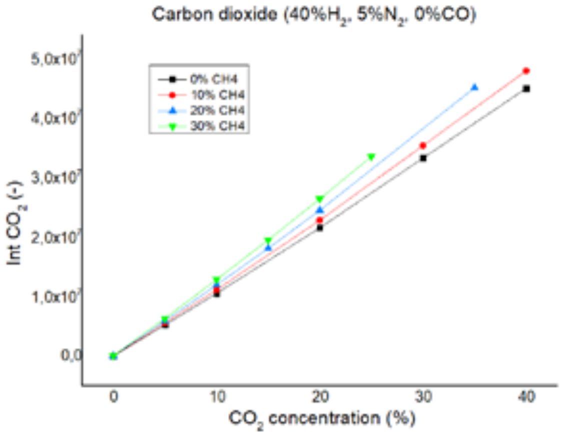

Fig.1. Variation of CO_2 peak intensity vs. concentration.

To solve this problem a more complex calibration has been tackled. Fig. 1 shows, as example, the relation between known CO_2 concentrations (“x”) and the response given by µGC (“y”) when other species (H_2 and N_2) are present, and CH_4 varies from 0 to 30 v%. CO_2 intensity increases when augmenting CH_4 in the sample, instead of showing a constant value for equal CO_2 concentrations. A matrix effect is observed in the analysis for every component.

GC peak intensity values are used as learning parameters for an Artificial Neural Network (ANN). In simple terms, ANN takes all the data to create a surface that adjusts to a non-linear behaviour and predicts a reliable outlet composition. The ANN has been modelled from a programming code using Python software. It consists of intertwined neurons that take the information given by the µGC on each experiment and carry out comparisons to determine the outlet composition based in previously learned patterns.

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Increasing the efficiency in the synthesis and functionalization of magnetic nanoparticles. Continuous mode of operation

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During the last decades, there has been growing interest in the use of magnetic nanoparticles (MNPs) due to their unique properties, including their high loading capacity, chemical stability and superparamagnetic behavior, which provides the particle a high response to the action of external magnetic fields; Applications of these particles in biomedicine, energy and data storage, catalysis and environmental remediation have been widely reported [1]. This work is in the framework of a research line focused on the development of high energy efficiency micro-magnetophoretic separations and has as one of its main objectives the synthesis of functionalized magnetic nanoparticles for the selective capture of solutes, such as chemical compounds or biomolecules, from different types of fluids [2].

Conventional synthesis methods present several hurdles, such as the design of reactors with suitable geometries, the appropriate control of operating conditions and the reproducibility and scalability. For this reason, the most recent strategy involves of the use of microfluidics to achieve a continuous and controlled synthesis of MNPs. Microdevices offer numerous advantages, most notably the possibility to work within a continuous process, the small residence times, improved mass and heat transfer and the positive environmental effects due to the reduced energy and reactants consumption. Moreover, variables such as microchannel diameter, residence time, reactant flow rates and temperature can be easily adjusted to obtain smaller particle sizes and narrower size distributions [1]. The MNPs synthesis procedure followed in this work consists of a co-precipitation reaction, followed by the surface functionalization of particles with primary and secondary amino groups, both steps taking place in a spiral shape microdevice (Circular section 3 mm, 400 mm length). The main properties of the particles were characterized by establishing their composition with Fourier transform infrared spectroscopy, measuring the particle size by transmission electron microscopy, calculating their level of functionalization from data obtained with Thermogravimetric and BET analyses, and determining the Z potential with dynamic light scattering techniques. Thus, Fe_2O_3 particles with an 8.7±1 nm diameter and a functionalization of 0.36 $\frac{\text{mmol amino group}}{\text{g particles}}$ have been obtained. They show a surface-charge potential which varies from positive values at acid pH to negative values at basic pH, with an isoelectric point at pH 8. Finally, the viability of the functionalized material is tested by means of experiments for the retention of hexavalent chromium present in aqueous solutions, selected as a model system [3].

Funding/Acknowledgements

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Comparison of technologies to synthesize polyethylenimine-citrate nanocomplexes as drug delivery vehicles for molecular targeting

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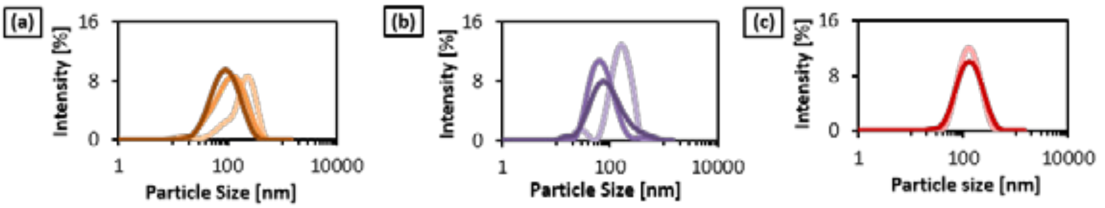
Nowadays, non-viral vehicles are acquiring great importance for drug delivery, especially in the form of nanoparticles of cationic biopolymeric materials such as polyethylenimine (PEI) or polycaprolactone (PCL) [1]. Antisense oligonucleotides (ASOs) are synthetic short-stranded RNA molecules and one of the most promising therapies for the treatment of neurodegenerative diseases, as spinal muscular atrophy (SMA) or amyotrophic lateral sclerosis (ALS) [2]. Delivering ASOs into affected cells requires the formulation of synthetic non-viral vehicles and their functionalization with cell markers, called aptamers, to enhance the selectivity of the targeted therapy. In our investigation, biopolymeric polyethylenimine-citrate (PEI-citrate) nanocomplexes were synthesized to deliver the ASOs targeted to muscular cells. Three different techniques were compared to achieve the highest cell transfection efficiency: (i) conventional nanoprecipitation method (NP), (ii) electrospraying (ES) and (iii) coaxial electrospraying (CA) (encapsulation of ASO). Fig. 1 (a-c) shows that the average particle size about 100 nm is similar in every technique employed. However, coaxial electrospraying presents more uniform reproducibility, probably because this configuration included the encapsulated ASO that could confer more electrostatic stability to the dispersion. Successful incorporation of the aptamer to the nanocomplexes can be confirmed by the sharp drop in zeta potentials to negative values of the functionalized PEI-citrate nanocomplexes.



Nanocomplex Structure	Zeta Pot.
NP	20±8 mV
NP/ASO	18±4 mV
NP/ASO/Ap	-12+2 mV

Nanocomplex Structure	Zeta Pot.
ES	27±8 mV
ES/ASO	23±4 mV
ES/ASO/Ap	-9±1 mV

Nanocomplex Structure	Zeta Pot.
CA (encapsulated ASO)	31±2 mV
CA/Ap	-10±2 mV

Fig. 1. Particle size distributions and zeta potential measurements of (a) nanoprecipitation, (b) electrospraying and (c) coaxial electrospraying

Assays of nanocomplexes transfection into C2C12 cells (mouse myoblasts) showed that the nanocomplexes prepared by coaxial electrospraying achieved the highest transfection efficiency. This result could be explained by the higher competence for active sites between ASO and aptamer in the surface of nanocomplexes by nanoprecipitation and normal electrospraying in comparison to coaxial electrospraying. Also, it was proved that the coaxial nanocomplex dispersion was the most stable over time. Further analysis on the performance of progressive ASO release into damage C2C12 cells will be pursued in the future.

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Pt-Zeolite composite membrane for water treatment

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Wastewater from chemical and pharmaceutical factories contains various organic substances. Persistent organic substances remain in the environment for a long time and some of them are toxic even in a low concentration. On the other hand, method that can treat wastewater containing harmful organic substances at low concentrations in an energy-efficient way is limited. Therefore, there is a need to develop new technologies.

In a catalytic membrane reactor (CMR), nano-sized catalysts are immobilized. CMRs have various advantages. For example, it does not require removing catalyst powder after water treatment. In addition, the CMR morphology facilitates the oxygen supply to the reaction field through a membrane, which enhances the oxidation of organic substances in water. It is reported that the organics in wastewater from dyeing factories, such as formic acid, was decomposed at 53 °C with an economically relevant speed [1]. On the other hand, the decomposition rate of phenols was slow [2]. It is necessary to find new catalysts for CMRs.

Zeolite can be used to host nano-sized catalysts in the zeolitic pores. Different types of composite powders have been reported. For example, metal-incorporated zeolite catalysts were reported to decompose dissolved organics such as formic acid and Rhodamine B under white light [3,4].

As described above, membrane morphology has various advantages. These metal-zeolite composites can be good candidates to improve the CMRs in water treatment. As a start, we investigated the influence of preparation conditions on the Pt-zeolite composite membrane performance in this study.

First, the synthesis conditions of the composite material were investigated in a powder form. Then CMRs were synthesized under the same conditions. The synthesized powders and membranes were analyzed using XRD/SEM/TEM/EDS. The catalytic ability of the composite materials was evaluated by the decomposition of formic acid dissolved in water. The concentration changes were analyzed by UV-vis measurement.

The metal-zeolite composite membranes decomposed formic acid in water at room temperature. The zeolite membrane morphologies affected the decomposition rate. Results showed that zeolite membranes can be used as a host of nano-sized catalysts for water treatment.

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Novel biopolymeric membranes functionalized with graphene-based nanomaterials for *in vitro* blood-brain barrier models

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There is huge interest in the development of useful *in vitro* blood-brain barrier (BBB) models (Fig. 1A) to help biomedical researchers and to save costs during the development of new drugs targeted to central nervous system. In our previous works, polycaprolactone (PCL)/graphene-based nanomaterials flat membranes improved the differentiation on neural progenitor stem cells [1].

In this work [2], PCL and PCL/graphene biopolymeric hollow fiber membranes (HFs) were synthetized by dry-jet wet spinning and characterized in terms of physicochemical, mechanical, electrical, and functional properties. Both PCL and PCL/Graphene (PCL/G) HFs exhibited high and interconnected porosity (Fig. 1B and 1C) and surface pore size higher than 0.5 µm, which are critical properties for the exchange of biochemical factors between cocultured cells in BBB models (Fig. 1A) [3]. The successful incorporation of graphene into the polymeric matrix significantly enhanced C6 cells differentiation towards astrocytes (Fig. 1D), maybe attributed to the higher electrical conductivity of PCL/G HFs, while graphene presence produced a cytotoxic effect on endothelial HUVEC cell line (Fig. 1E).

The results highlight the need of developing a dual-layer porous HF membrane, i.e. internal PCL layer and external PCL/G layer, to favor simultaneously the proliferation of HUVECs and C6 differentiation for the future development of a dynamic *in vitro* BBB model.

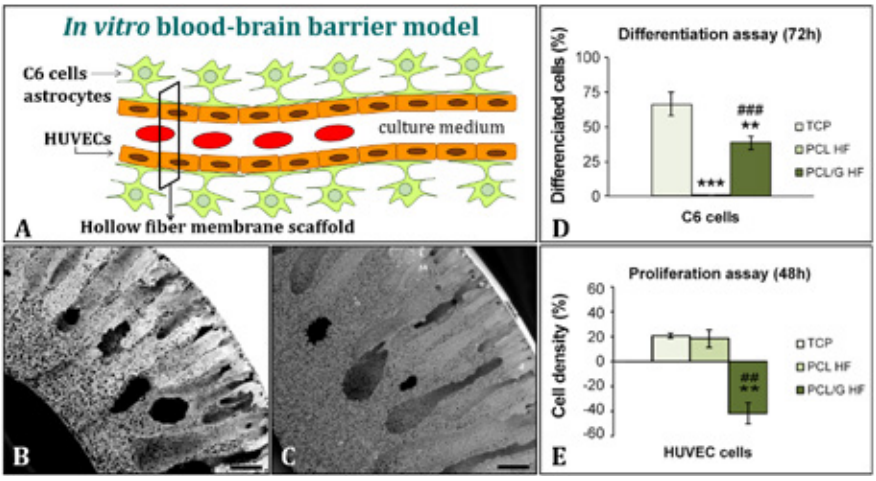

Fig. 1. A) Schematic development of an in vitro BBB model in HF membrane. ESEM cross-section images of B) PCL and C) PCL/G HFs. Quantitative results of D) C6 cells differentiation and E) HUVEC cells proliferation on TCP, PCL and PCL/G HFs; **, ## $p < 0.005$; ***, ### $p < 0.0005$ vs TCP and PCL ($n = 4$ per group; one-way ANOVA with Bonferroni correction). Scale bar: (B, C) 50 µm.

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Tuning the fabrication of polymeric hollow fibers for different applications in Chemical and Biomolecular Engineering

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Porosity and pore size are critical factors affecting membrane functional properties and applications. Hollow fiber (HF) membranes are usually processed by dry-jet wet spinning, in which the synthesis variables must be tailored to tune the morphology [1]. However, depending on the polymer system and the setup configuration, the flexibility to change variables affecting the precipitation rate is low. In this work, polyvinylidene fluoride (PVDF) polymeric HFs were produced. The influence of doping the polymer solution with polyethylene glycol (PEG) and isopropyl alcohol (IPA) was analyzed as well as the influence of bore liquid fluid composition and coagulation bath; the rest of variables, i.e. air gap and flow rate of the polymer solution and bore liquid, remained constant.

In this work, changes between using 100% water or 80/20 v/v % water/IPA in the coagulation bath or in the bore liquid did not produce significant changes in the membranes morphology. Therefore, the main factor affecting the morphology of the HFs was doping a fourth component in the polymer solution, which altered drastically the thermodynamics and kinetics of the phase inversion system. Three main groups of HFs can be identified aimed at different applications. The first HFs group (not doped) is considered suitable for ultrafiltration, i.e. protein separation (Fig.1 a and d) with a 11.2 L·bar^{-1}·m^{-2}·h^{-1} hydraulic permeance. The second group (PEG doping, Fig.1 b and e) presents open porosity with 280.4 L·bar^{-1}·m^{-2}·h^{-1} permeances more typical for microfiltration which can assure nutrients and metabolites exchange i.e. in perfusion bioreactors for tissue engineering. Finally, the third group (IPA doping, Fig.1 c and f) with a denser morphology than the rest and the lowest hydraulic permeance, 4.2 L·bar^{-1}·m^{-2}·h^{-1}, might be appropriate as a support to be further coated with a selective layer for gas separation.

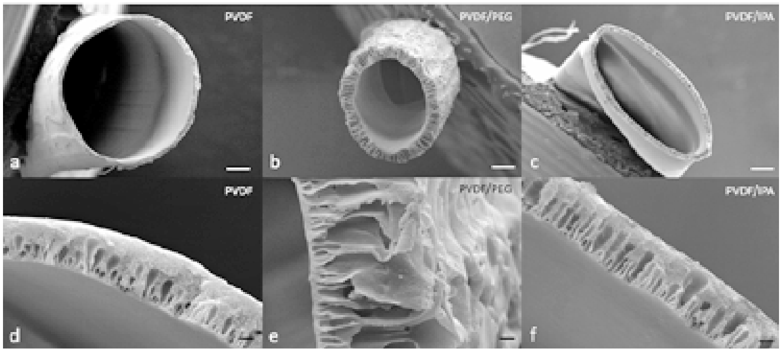

Fig. 1. SEM images of the different HFs synthetized. HFs for (a, d) ultrafiltration application, (b, e) tissue engineering application, (c, f) gas application. Scale bar: (a-c) 100 µm, (d-f) 10 µm.

Future work will be focus on testing specific separation performance of the HFs for each of the applications discussed above, i.e. the filtration of a model aqueous solution of the protein bovine serum albumin (BSA) to determine nutrients permeance for perfusion bioreactors.

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Synthesis and characterization of composite antibacterial anion exchange membranes for reverse electrodialysis applications

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Reverse electrodialysis (RED) is a membrane-based technology that generates electrical power by water streams with different salinities [1]. The development of the antibacterial anion exchange membranes (AEMs) is critical in RED applications because the bacteria create a permanent fouling layer on the AEMs surface and cause the loss of their performances. Since microorganisms such as bacteria cannot penetrate into the inner structure of dense and non-porous AEMs, thus only a modification on the surface of the membranes will be sufficient.

This work aims to synthesize the AEMs with antibacterial behavior by immobilizing silver nanoparticles (AgNPs). For this purpose, the polyepichlorohydrin (PECH) polymer was quaternized by 1,4-diazabicyclo[2.2.2]octane (DABCO) to produce AEMs. The AEMs were prepared with solution-casting method followed by the solvent evaporation technique [1]. The AgNPs were produced at 30 °C using ascorbic acid (AA) as a reductant and trisodium citrate (TSC) as a stabilizer at pHs 6.0 and 9.0 [2]. The AgNPs were immobilized onto the AEMs by dip-coating method to obtain composite membranes. The XPS analysis was performed to determine the chemical components on the surface of the membranes. The SEM-EDX mapping and XRD analyses were used to observe the distribution of the AgNPs on the surface of the AEMs. Antibacterial activity of the AEMs was determined with the colony-counting method using model gram-negative (Escherichia coli) bacteria suspension. The results indicated that the AgNPs immobilized AEMs showed a high antibacterial activity. As expected, the presence of O, Ag, N, C, and Cl elements on the surfaces of the AEMs was demonstrated by the XPS analysis. The SEM and EDX mapping results showed that homogeneous distribution of the AgNPs was observed on the surfaces of AEMs at pH 6.0, while AgNPs agglomerations were formed at pH 9.0. The present study showed that AEMs with antibacterial activity were successfully synthesized for the RED applications by immobilizing the AgNPs onto the membrane surface via dip-coating method.

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High performance membranes for hydrogen recovery from industrial waste streams. Towards processes energy efficiency

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Hydrogen, which is a sustainable and greenhouse emissions free energy source, can be widely found as feedstock or co-product in the industry. This situation results in the emission of 0.5 million tons H_2 per year into the atmosphere, in the form of purge streams such as, ammonia and methanol purge gas or co-product such as the coke oven gas. Thus, the recovery of residual hydrogen is positioned as a great niche of opportunities with the aim of reducing the energy consumption and therefore, the environmental impact and operational cost of industrial processes. Nevertheless, due to the high purity requirements of hydrogen applications as energy vector, it is necessary to use a separation technology for the purification of hydrogen. In this sense, membrane technology has received great attention in recent decades due to its low installation cost and low energy consumption, its modularity and good separation performance. Although the several commercially available alternatives in the market, the research and development of tailor-made, hydrogen-selective membranes together with obtaining high production flows is essential to achieve its industrial implementation. The incorporation of selective hydrogen additives (zeolites or Metallic Organic Framework, "MOFs") during the synthesis process of high-flow polymer membranes, has given rise to "mixed matrix membranes" which are a novel alternative with the aim of improving the separation performance of pristine polymer membranes. The addition of ZIF-8 and ZIF-90 to hydrogen selective polymer (Matrimid®, polyimide) is being analyzed in the frame of this doctoral thesis.

The mixed matrix membranes were prepared by solving-casting method (flatsheet configuration) and by the well-known wet-spinning process (hollow fiber configuration). The polymer and the additive were weighted at different compositions (0 to 20% of ZIF). Then, the polymer and additive were dissolved in an organic solvent (flatsheet: dichloromethane, hollow fiber: N-Methyl2-pyrrolidone) and stirred overnight. The solution was also sonicated 2h to prevent the agglomeration of the ZIF particles. The mixture was then poured over the surface of a Petri dish in the case of flasheet membranes or extruded in the case of the hollow fibers.

The separation performance of the mixed matrix membranes was tested in permeation experiments with pure gases and multicomponent gas mixtures whose composition correspond to those of the industrial waste streams. The membrane module was placed in a thermostatic chamber to ensure isothermal operation (30, 50 or 80 ºC). Moreover, the composition of the permeate and retentate streams was real-time measured by gas chromatograph (Tracera GC-2010) equipped with a Barrier Ionization Discharge (BID) detector of ppb quantity level. Results showed higher hydrogen permeability (from 20 to 50 Barrer) and selectivity (from 2.6 to 4, H_2/CO_2) in the mixed matrix membranes than in the case of pristine Matrimid® membranes.

Funding/Acknowledgements

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Counteracting SAPO-34 catalyst deactivation in MTO process using a two-zone fluidized bed reactor

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Olefins are a key building block in chemical industry and their worldwide demand increase motivates research on new routes and processes. Traditionally, olefins are obtained via steam cracking of distillates from crude oil, but in the last 40 years, new processes of production have been studied. One of the most promising one is the methanol to olefins (MTO) process, in which crude oil is substituted by methanol as raw material [1]. This alternative process offers the use of a greener raw material, methanol, which can be obtained by reaction of CO_2 (from carbon capture processes) and H_2 (from water hydrolysis).

The main drawback of MTO is the fast deactivation that the catalyst suffers. Usually, this catalyst is based on the SAPO-34 zeolite, which deactivates rapidly by coke deposition due to its small pore size [2]. To face this problem, a two-zone fluidized bed reactor is proposed (Fig. 1). In this device, reaction and regeneration of the catalyst take place continuously in the same vessel, which avoid the need of additional regeneration steps after reaction [3].

The reactor has two feeding points, one at the top of it, for which methanol and a carrier gas are fed, and one at the bottom, where the regeneration agent (usually O_2) and a carrier gas are fed. The division between reaction and regeneration zones is determined by the methanol feeding point, which can be adjusted by the height of a T shaped quartz rod. In this point, reaction and regeneration gases are mixed up, which implies that both zones are not totally independent one from another.

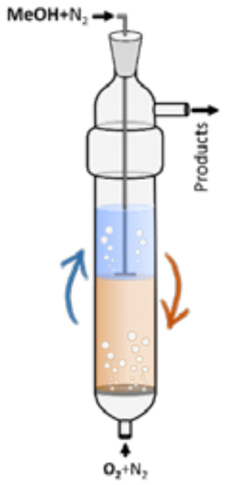

Fig. 1. Two zone fluidized bed reactor scheme.

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Composite hollow fiber membranes for O_2/N_2 separation from Air by gas permeation

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In recent years, the need to reduce energy consumption worldwide to move towards sustainable development has led many of the conventional technologies used at the industry to evolve or to be replaced by new alternatives. In this way, separation of oxygen and nitrogen from air has become a high interest separation due to the wide range of applications both have at industrial and medical level. To date, the most widely used techniques to perform this separation are cryogenic distillation and pressure swing adsorption (PSA). Both can reach purities of 95-99% and large productivities, but requires high capital investment and are highly demanding in terms of energy consumption and are only cost-effective on a medium to large scale [1]. Thus, a new emerging method of oxygen/nitrogen separation that has gained importance in recent years is membrane separation due to it allow overcoming many of the barriers that traditional technology has. One way to make membrane technology competitive is the implementation of hollow fiber membrane modules, instead of the current flat-sheet membrane modules [2].

In this sense, the aim of this work is to develop cost-effective advanced multilayer hollow fiber composite membranes made of Matrimid and polydimethylsiloxane (PDMS) for the separation of oxygen and nitrogen from air. The technique used for the manufacture of hollow fiber membranes is spinning, through which Matrimid is extruded with the help of a spinneret. Subsequently, a very thin PDMS layer can be added by the dip coating method, and finally, a module is manufactured with the hollow fiber membranes ready for testing. Among the main results of the work is the successful fabrication of Matrimid hollow fiber membranes. This membrane has a porous sponge-like inner layer that does not exert any resistance to separation and a thin dense outer layer, thanks to which the separation takes place. In addition, a cover layer of PDMS was deposited on the membrane by dip coating to improve the membrane performance, reaching O_2 permeabilities of 350 Barrer and an O_2/N_2 selectivity of 5 (60°C). This makes them among the best in the literature.

Funding/acknowledgments
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UV-C LED reactor for a more sustainable disinfection and remediation of wastewaters

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Wastewater treatment plants (WWTP) may constitute a source of contaminants of emerging concern (CECs) release into the environment (pharmaceuticals, personal care products, herbicides, pesticides…) and microbiological elements (bacteria, virus…). Many of these CECs can accumulate in sediments and biota and lead to chronic and toxic effects for humans and ecosystems even when released in low concentrations (ng/L or µg/L) [1]. Therefore, it is necessary to implement more effective treatments before treated wastewaters are discharged to the environment.

Traditionally, photo-assisted disinfection has been carried out using medium or low-pressure mercury lamps as irradiation source working in the UV-C range. Despite this technology is widely known, it requires frequently lamp replacement, it uses toxic mercury, and its lifetime is shortened with each lamp operating cycles. For this reason, the performance of a new UV-C LEDs (light emitting diodes) reactor with a maximum emission wavelength at 278nm is being studied. Its potential for pathogens removal with simultaneous photolytic degradation of some organic compounds has been reported [2]. Moreover, the high energy requirements and other technical issues of conventional UV-C lamps could be overcome thanks to the use of new LEDs technology.

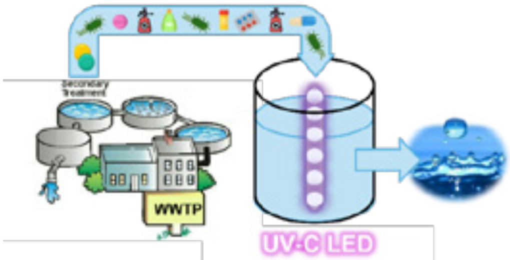

Fig. 1. Explanatory diagram of the UV-C LED process.

Two selected CECs (dexamethasone and S-metolachlor, which are used as pharmaceutical and herbicide, respectively) and bacteria (*Escherichia coli*) were effectively degraded by photolysis. Their removal followed first-order kinetics but their apparent rate constants were very different. Moreover, the required dose for disinfection was about 500 mJ/cm^2 whereas the organic compounds needed 2160 mJ/cm^2 in the best case, without achieving any mineralization. Simultaneous disinfection and degradation were further enhanced using additional oxidants such as H_2O_2. Moreover, the comparison of the different processes in terms of energy and cost is being carried out with some figures of merit such as the electrical energy per order (EEO), with values from 1.5 kW/m^3·order for bacteria to 9.3 for the best case of organic compounds.

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Dicarboxymethyl cellulose and its applications

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Cellulose is one of the most abundant polysaccharides on Earth. Environmental awareness has led to an increase in the scientific interest in this material and its derivatives. By developing new materials through the functionalization of cellulose, resource availability is overcome. Moreover, cellulose derivatives can be designed for a broad field of applications, while providing a sustainable alternative to petroleum-based materials [1].

Dicarboxymethyl cellulose (DCMC) is produced by the heterogeneous etherification of cellulose with a halogenated malonate. This cellulose derivative can perform cation exchange at low pH (2.5-3.5), making it suitable for various applications (Fig.1) [2].

DCMC has been successfully used in the adsorption of methylene blue from aqueous solutions. This experiment suggests this polymer may be useful in the treatment of wastewaters containing dyes [2]. The polymer may also be applied to protein adsorption (cytochrome C, thaumatin). White wine protein stabilization requires a fining agent that removes haze-forming proteins. Bentonite fining, the predominant method, presents several drawbacks, including lees formation and loss of wine. DCMC fining has been shown to reduce white wine protein content and turbidity [3]. This has the potential to contribute to a more sustainable process in the winemaking industry.

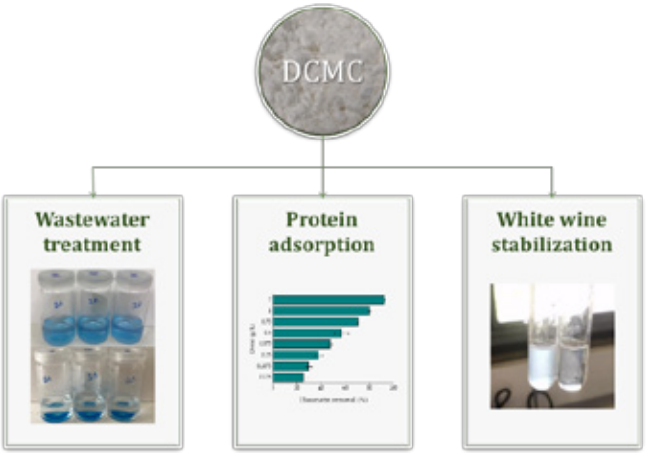

Fig. 1. Schematic illustration of the applications of dicarboxymethyl cellulose.

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Green hydrogen-based power system for social housing decarbonization

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Introduction

The reduction of greenhouse gases (GHG) emissions to mitigate climate change requires the implementation of various measures, such as the replacement of fossil fuels by renewable energy sources (RES), the increase in the efficiency of the systems, implementation of carbon, capture, storage, and utilization (CCSU) technologies to decarbonize the use of fossil fuels and switch to zero-emissions energy carriers. Thus, hydrogen has emerged as a clean and versatile energy carrier that ensures a higher RES penetration that is fundamental to achieving the required energy transition [1,2]. In this context, the SUDOE ENERGY PUSH project combines RES, novel hydrogen technologies, building information modelling (BIM) methodology, and passive renovation to improve the energy efficiency of social housing in the regions of southwestern Europe [3].

Methodology

As part of the project, a pilot plant to produce green hydrogen to supply a social home is designed. This pilot plant employs photovoltaic (PV) panels as the primary energy source to power the household. Then, two different energy storage systems are integrated to ensure independence from the utility grid: batteries for short-term energy storage and hydrogen for seasonal storage. First, the batteries accumulate the energy excess from the PV panels. When they are charged, hydrogen is generated from water electrolysis in an electrolyzer and stored in a pressurized tank. Finally, if there is not enough solar resource or sufficient battery charge, a fuel cell generates electricity on demand from the stored hydrogen.

Major findings

Thanks to the pilot plant implemented within the framework of the project, the home can be disconnected from the grid, saving up to 7,000 kWh per year of primary energy from the grid and 1,000 kg per year of CO_2 emissions while consuming 100% clean electricity.

Funding/Acknowledgements

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Low-cost membrane bioreactor for wastewater treatment

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Membrane biological reactors (MBR) constitute an alternative to conventional wastewater treatments for improved recovery, reuse, and recycling of water. MBRs have a smaller footprint, provide better biotreatment and achieve a high-quality effluent [1]. This work analyses the use of MBRs with low-cost ceramic membranes as an alternative to the higher cost of commercial ceramic membranes [2]. These were made of clay, calcium carbonate, potato starch, almond shell and chamotte. Two different selective layers were synthesized from clay (M_Almond_Clay55) or TiO_2 (M_Almond_TiO_2). Membrane characterization was completed by determining water permeation and pore size. For the last one the bubble point method was used.

Table 1. Water permeance, bubble point and average pore size (d_{50}) for membranes

	Water permeance ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	$d_{bubble\ point}$ (μm)	d_{50} (μm)
M_Almond_Clay55	1321	13.9	3.0
M_Almond _TiO_2	731	2.89	0.5

The experimental setup consisted of a cylindrical PVC tank with a volume of 30 L equipped with two air diffusers. The submerged flat sheet ceramic membrane (area = 0.032 m^2) was placed between two baffles that simulated parallel membranes. The inoculum was activated sludge from an urban wastewater treatment plant. The bioreactor operated with synthetic wastewater and it was feed with a pump. The permeate was withdrawn with a pump at a constant flux of 15 $L \cdot h^{-1} \cdot m^{-2}$ and to carry out the membrane backwashing another pump was used. Different operation cycles were studied, and the optimum was: 9’permeate – 30’’relaxation – 30’’backwashing. The effect of air scouring on fouling was investigated operating with different air flowrates. Increasing the air flow rate in the membrane area resulted in lower fouling rates but at high cost. To reach a compromise between fouling and costs, an air flow rate of 700 $cm^3 \cdot min^{-1}$ was selected. Once experimental conditions were optimized, the overall performance of both membranes was tested. The membrane M_Almond_TiO_2, was able to operate without exceeding a transmembrane pressure of 0.1 bar in one month and exhibited the highest quality of the effluent (DQO < 30 mg $O_2 \cdot L^{-1}$). Also, the retention capacity of *Escherichia coli*, *Cryptosporidium* oocysts and *Giardia* cysts [3] of the ceramic membranes was evaluated, obtaining a retention efficiency of 99.99% in all cases.

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Continuous-flow micro-reactors with curved geometries. Experimental and numerical analysis

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Microfluidics have recently attracted great attention among the scientific community due to their unique capabilities in the control of molecules concentration in space and time offering new opportunities in multiple fields. However, there is still need to improve the performance of these devices when very fast reactions are carried out and the results could be compromised by the poor mixing efficiency of the reactants [1].

This work, aims at reporting a holistic analysis of reactants mixing and reaction rate in liquid phase flow micro-reactors with curved geometries. In this sense, a mathematical model that accounts for momentum and mass conservation equations, together with species transport and chemical reaction rate under isothermal conditions, has been developed using computational fluid dynamics techniques (CFD). To validate the predictive model, four micro-reactor geometries have been designed with different radius and curved length. Simulated results proved that mixing is promoted through the formation of Dean vortices consequence of reducing the curvature radius and at the same time increasing the curved-length. Thus, the overall performance of the micro-reactor is improved, minimizing the mass transport limitations. Accordingly, the spiral flow micro-reactor achieved the best performance (Fig. 1a) reducing by half the time required to obtain 95% conversion compared with the straight reactor. Simulated findings have been confirmed with the experimental analysis of the reaction between aqueous ammonium and hypochlorite ions. Outstanding fitting between simulated and experimental results has been achieved with an error lower than 10% (Fig. 1b). Therefore, the robust model herein reported is a novel and valuable tool to assist in the optimum design of micro-reactors for fluid-phase isothermal applications.

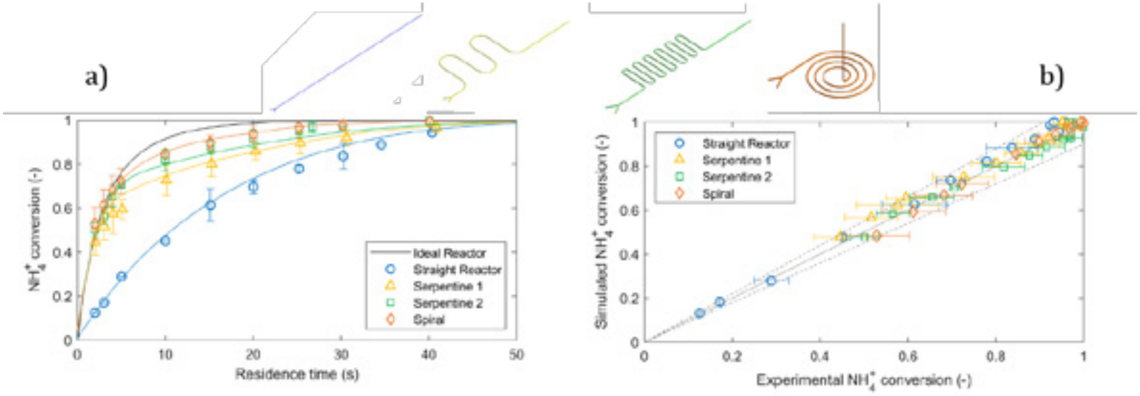

Fig. 1. a) Ammonium conversion as function of the residence time in the micro-reactors and b) parity plot with a ±10% error between the experimental values and the mathematical model simulations for different micro-reactor geometries.

Funding/Acknowledgements
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Copper oxide-based nanosponges microstructures for glucose detection

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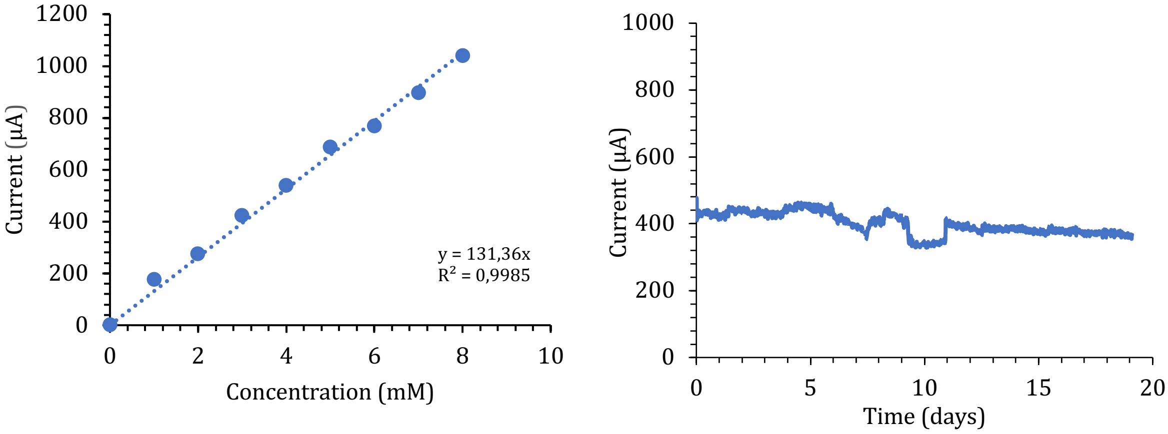
Nowadays almost 600 million people between 20 and 79 years old are suffering from *Diabetes mellitus*. The most common preventive method for this non-communicable disease is the finger pricking which is considered invasive since it requires long detection times and blood extractions. Thus, great efforts are currently focused on the obtention of long lasting, stable, and non-invasive devices. This work presents the development of a non-enzymatic glucose sensor based on copper oxide microstructures through a reproducible and robust method. The sensor is competitive with existing commercial devices since shows a lifespan of 18 days (measurements each 5 minutes) within a relative standard deviation (RSD) of 8%, which meets the ISO 15197 requirements. The characterization of the nonenzymatic biosensor was addressed by studying the sensitivity, active area, reproducibility, repeatability, stability and performance under common biological interferences; *uric acid, ascorbic acid, ibuprofen and chlorine.* Fig.1 presents the results for sensitivity and lifespan.



The reported electrode presents a step forward with respect to the current state-of-the-art [1]. However, although these results represent a large progress in the diabetes preventive methods field, more efforts are still required for the development of electrodes sensitive at physiological conditions, especially pH.

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Gas permeation applied to CO_2/CH_4 separation using chitosan-based and polydimethylsiloxane membranes

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Membrane separation processes are a great alternative to address the drawbacks of amine processes for CO_2 capture and biogas upgrading where the effective separation of CO_2 and CH_4 is crucial [1]. However, commercially available membranes still face challenges regarding water and chemical resistance [2]. Chitosan (CS) is a non-toxic, hydrophilic, functional, biodegradable and biocompatible polymer from abundant natural sources, with good adhesive and film forming properties whose primary amine and hydroxyl groups exhibit strong affinity towards CO_2, in humid streams.

The present work evaluates the gas permeation performance CS-based composite membranes for the separation of CO_2/CH_4 mixtures, to identify the optimal design and operation conditions that maximize the technical performance, given in terms of purity and recovery of components, as a tool to advance in parallel in the implementation of the membrane separation systems and the development of membrane materials. IL-CS/PES membranes were prepared by coating CS layer hybridized by 5 wt% [emim][acetate], a non-toxic ionic liquid (IL) with high CO_2 affinity, on porous polyethersulfone support. In addition, to increase permselectivity, different mixed matrix membranes (MMM) with inorganic fillers are also considered [3]. In order to improve the permselectivity of IL-CS/PES membranes, layered silicate fillers and HKUST-1 MOF have been used to hybridize the coated layer.

The permeance and selectivity parameters were measured at laboratory scale and introduced to the membrane unit mode. The sensitivity analyses showed that increasing the stage cut (from 0.1 to 0.9) for the different membranes increases CO_2 recovery while decreases purity in the permeate stream. The opposite happens with CH_4, the key component in the retentate stream. The performance of commercial polydimethylsiloxane membranes was measured as reference. The CS layer improves the purity of CO_2 and CH_4 over the whole range of CO_2 and CH_4 recovery.

The counterbalance observed between the objectives (purity and recovery of the gas components in permeate and retentate) reflect the need to consider both CO_2 and CH_4 products for the technical optimization of the separation. Multi-objective optimization can help the minimization of the normalized distance for all the objectives.

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ABE fermentation for butanol recovery by Pervaporation

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The interest in fermentative production of n-butanol from renewable 2nd generation biomass is currently increasing. n-Butanol is an industrial solvent that can be used as a substitute for gasoline or jet fuel. Some bacteria are able to secrete enzymes that convert simple sugars into organic acids and finally into alcohols, through acetone-butanol-ethanol (ABE) fermentation. Yet, the very low conversion yield providing low product concentration, the severe solvent toxicity to microorganisms and the high-energy demand are still some challenges that prevent the process from being more competitive over the petrochemical route. In this work, glucose conversion was accomplished by pH-controlled batch fermentation in a defined medium to set the parameters for the fermentation of complex biomass into butanol that will be recovered by Pervaporation (PV) [1]. **Methods.** The batch fermentation assays with C. butyricum were performed in serum bottles with basal modified medium (BM1) reproduced as in [2], with 2 g L^{-1} of glucose and 10% (v v^{-1}) inoculum. Incubation proceeded for 72 hours at 37 °C. Three replicates were prepared for each sampling (every 24h) and the results were expressed as mean ± standard deviation (SD). Fermentation performance was assessed through: HPLC for glucose, acid and solvent quantification; pH monitoring; microscopic observation and quantification of the produced biogas. **Results.** During the acidogenic phase (exponential growth phase), the pH lowered due to the production of acetic, butyric, lactic and propionic acids. During the solventogenic phase, the pH increased slightly due to the production of alcohols from the organic acids, but to a value below that of the initial BM1 media (Fig. 1). About 10-12 mL of biogas, containing H_2 and CO_2, were produced along the experiment.

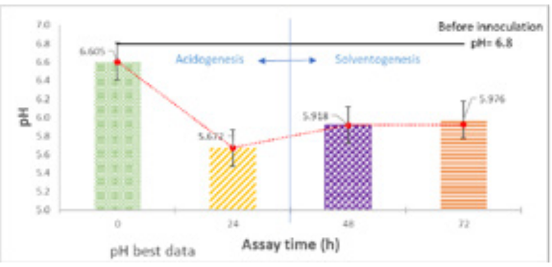

Fig. 1. Acidogenic and Solventogenic phases accomplished by *Clostridia butyricum*.

Conclusions. The conditions for ABE fermentation by butyricum were implemented. Oganic acids and H_2-rich biogas were obtained as coproducts. The fermentation profile obtained will be used to set the parameters and guidelines for butanol production in bioreactor and the future strategy for process integration with membrane separation technology by PV, targeting process intensification.

Funding/Acknowledgements

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Sorption-enhanced CO_2 methanation process based on a bifunctional Fe-Ni catalyst

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Abstract

An intensification in *Power to Gas* (PtG) technologies is proposed as an alternative for energy storage. A catalytic Fixed-Bed reactor was selected and different catalysts were tested, being found as the optimal one a Ni-Fe (7.5:2.5 $^{wt}/_{wt}$) supported in (γ-Al_2O_3). An important improvement based on water adsorption was observed by using LTA zeolites in the bed.

Introduction

Power to Gas technologies (PtG) are based in using surplus energy obtained from renewable sources to generate green H_2 by water electrolysis [1]. On this way, hydrogen is used to transform CO_2 captured from sequestered emissions or biogas (30%^{v} CO_2 + 70%^{v} CH_4) into sustainable methane. So, called *Synthetic Natural Gas* (SNG) could be used as an energy vector. Also, this product can be transported and supplied using the preexisting natural gas network. Methanation process is based on the *Sabatier* reaction (r.1) [2].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_r^0 = -165.1\ \text{kJ/mol} \quad \text{(r.1)}$$

A catalytic Fixed-Bed reactor was chosen for intensification of the PtG process. Traditionally the more often used catalytic species in (r.1) are ruthenium and nickel. The high cost of ruthenium is a limiting factor for the industrial scale up of methanation. On the other hand, higher amounts of nickel are needed to obtain a similar methane conversion than ruthenium catalyst. Thus, one of the main goals in the intensification of methanation process is to develop an economic alternative for the conventional catalysts. The use of water adsorbent solids in order to *in situ* remove the water produced by (r.1) is another option analyzed.

Results and conclusions

A lab made bifunctional catalyst based on a combination of iron and nickel supported on alumina (γ-Al_2O_3) Ni-Fe (7.5:2.5 $^{wt}/_{wt}$) shown conversion values close to ruthenium one. Including a second metal as iron, makes catalyst costs to decrease. Also, the presence of iron allows reducing catalyst deactivation by coking. Finally, mixing the catalyst with appropriate adsorbent can push up the conversion of reactants, even beyond the equilibrium.

Funding/Acknowledgements

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Photocatalytic Decomposition of organics by $AgTiO_2$ membrane

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Water treatment with photocatalysis is a nontoxic and economical process. Treating dilute organic pollutants dissolved in wastewater can be problematic if the compounds are persistent and not biodegradable. This study proposed an application of $AgTiO_2$ membrane for this purpose. TiO_2 is a nontoxic and stable photocatalyst. Silver is also nontoxic with antibacterial properties. Depositing silver on TiO_2 membranes by photoreduction method increased the bare TiO_2 membrane performance by inhibiting electron-hole recombination. At low silver concentration, $AgTiO_2$ membrane showed a remarkable increment in photocatalytic oxidation of diluted formic acid. From TEM images and EDS mapping, the deposition of high amount of silver on the membrane was found to cause agglomeration of Ag nanoparticles and, at the same time, a reduction in photocatalytic performance was observed. In addition, the role of silver as electron sink seems to be eliminated in the presence of salts. The performance was reduced by 50% with 0.1M NaCl and further reduced up to 70% with 0.1M $MgSO_4$. The performance was comparable to 0.05M $MgCl_2$ and 0.1M K_2SO_4, pointing out that SO_4^{2-} hindered the activity more severely than Cl^-.

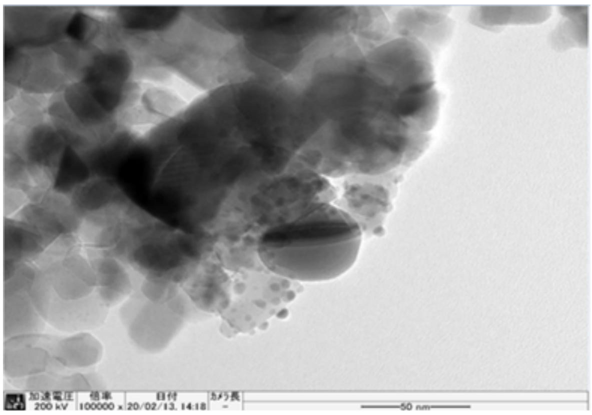

Fig. 1. Deposited silver on TiO_2 by photoreduction method.

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Expression repression of a designed gene and its release by introns

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Gene design technology

Currently, useful proteins are widely utilized in our life, for example, food- production and biopharmacy. These useful proteins have been produced by transgenic organisms. However, the proteins that are produced in large quantities are limited. To increase protein production, gene design technology has attracted much attentions, in which nucleotides are arranged to encode any desired amino acid sequences. Several genetic design rules for protein-production are reported, for example, RNA secondary structure [1] and codon optimization [2]. However, still not all proteins are produced efficiently, suggesting that the rules for gene design are not yet fully understood.

A problem in a designed gene

We expressed wild-type (hCLuc) and yeast-codon-optimized (yCLuc) Cypridina luciferase genes and compared their production levels in yeast. Unexpectedly, despite the codon-optimization, yCLuc protein production was 1/40 of hCLuc (Fig. 1a). The amino acid sequence encoded by the genes are completely identical. In addition, the secondary structures of the RNAs do not have clear difference. Therefore, the result suggested presence of an unknown problem in gene design of yCLuc. To elucidate the problem, we constructed and analyzed chimeric genes consisting of yCLuc and hCLuc (Fig. 1b). As a result, we found that 100 to 150 bp sequence of yCLuc repressed its expression.

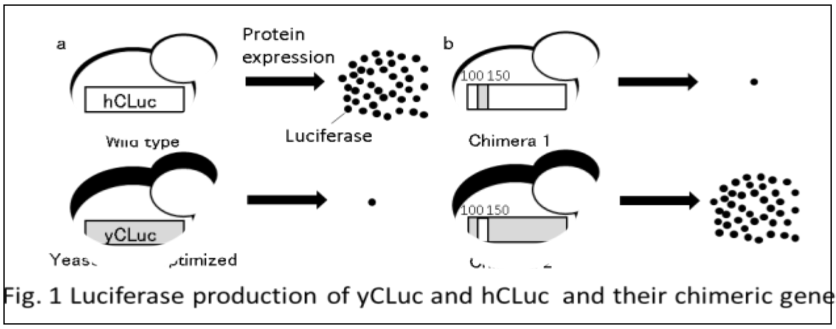

Fig. 1. Luciferase production of yCLuc and hCLuc and their chimeric genes.

Rescue from repression by intron

It is known that protein production is increased by inserting an intron into a gene [3]. This is called Intron-mediated enhancement (IME). We tested the effect of intron on luciferase expression. As a result, expression of yCLuc was enhanced by an intron. On the other hand, hCLuc expression was not. This result suggest that IME may be a mechanism to rescue genes from expression repression which is caused by nucleotide sequence.

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Theoretical and practical approach to the dealcoholization of red wine by osmotic distillation

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Viticulture has been affected by the climate change, whose impact on the annual cycle of wine leas to an increment of 2%v/v of ethanol in wines. Besides, the growing social tendency towards a healthy lifestyle avoiding an excess of alcohol consumption, has resulted in an increasing demand of wines with lower ethanol content. In this context, osmotic distillation (OD) has been a subject of interest due to its promising application in the production of low alcohol strength wines. This work focuses on the partial dealcoholization (-3 v/v%) of red wine by OD, carrying out an experimental and theoretical process approach. The dealcoholization process was performed using a polypropylene hollow fiber module at different experimental conditions to evaluate their influence in the ethanol behavior. At the best tested conditions, the study of the behavior of ethanol and other five different alcohols (both aliphatic and aromatic) and their transport mechanism through the membrane was carried out. As a result, a transport resistance expression, where the volatility of the compounds (Henry’s constant) and their interaction with the membrane (in terms of Hansen solubility parameters) were included, was successfully developed. This allowed reducing the error between the experimental and theoretical alcohols concentrations in a relatively wide range of working conditions.

Funding/Acknowledgments

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Magnetophoretic Separations as More Efficient Technologies for the Recovery of Target Solutes

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Current challenges of downstream processing call for the development of novel strategies that promote the efficient recovery of the target compounds from the reaction media. For that purpose, magnetic separation has received outstanding attention, since it entails a reduction of the costs and an increase of the productivity compared to conventional separation techniques. From the different platforms where magnetic separations can be carried out, microfluidic devices, which meet the criteria of process intensification through miniaturization, offer outstanding possibilities. Therefore, the retrieval of target compounds labelled with magnetic beads in magnetophoretic microseparators is currently understood as a promising strategy.[1,2] However, further investigations about the most appropriate magnet arrangement are required in order to increase the magnetic gradient exerted on the beads, thus, optimizing magnetophoretic microseparations. Herein, we compare the performance of two magnetophoretic microseparators, with similar geometrical features, that are typically used for bead recovery purposes: (i) annular channel with a quadrupole orientation of the permanent magnets, named as QMS, and (ii) standard design, which comprises a rectangular channel with a single permanent magnet [1,2]. To this end, we introduced an experimentally validated computational fluid dynamics (CFD) numerical model, using the commercial software package *FLOW-3D*. Our results reveal that the QMS, compared to the standard design, could fulfill complete bead recovery while (i) treating more than 360 times higher flow rates or (ii) retrieve smaller particles, which entails a 55% reduction of the particle mass. Collectively, this work demonstrates the improved performance of QMSs and demonstrates their potential in the intensification of magnetic bead recovery.

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Effect of volatile acids in fermentation broth on the ethanol-selective property of a silicalite-1 membrane

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Together with a group at the faculty of agriculture at our university, we have been trying to develop an energy-efficient, environmentally friendly and simple process to convert inedible feedstocks to fuel. The group at the agriculture faculty has been working on high-temperature fermentation. This is a fermentation operated about ten degree higher than a general one. While high-temperature fermentation has a potential to improve the conversion efficiency, it can only produce dilute ethanol (<10%). Accordingly, a process to concentrate ethanol is required after fermentation. Commonly, distillation and azeotropic distillation are used to bring ethanol concentration over 99% but this process consumes huge energy. Replacing distillation with a membrane separation can reduce the energy consumption about 65%.

This study focused on the development of hydrophobic membranes to concentrate a dilute ethanol solution after fermentation to over 80%. Membrane performances are often evaluated with a synthetic binary mixture. In this study, we investigated the effect of volatile components in the fermented solution on the membrane.

Silicalite-1 membranes were prepared by hydrothermal synthesis on porous ceramic tubes. Membranes were characterized by X-ray diffraction analysis (XRD) and pervaporation (PV) using a synthetic ethanol solution and a distillate of a high-temperature fermentation broth (FS solution).

The permeate of silicalite-1 membrane contained about 80% ethanol when 13% ethanol solution was applied to the membrane at 60°C. The flux was about 1.4 kg m^{-2} h^{-1}. The membrane concentrated ethanol when a FS solution was applied, but the flux was reduced to 20% compared to the flux obtained with a synthetic mixture. No significant changes were observed by XRD analysis after these tests, indicating the robustness of silicalite-1 material in the FS solution. The flux was recovered by heat treating the membrane at 500°C. These results suggest that the adsorption of contaminants in the FS solution reduced the flux. Possible reasons and a method to prevent the flux decline are under study.

Carbon emissions in Uzbekistan: problems and solution

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Carbon dioxide as an emission of greenhouse gas is the main contributor to climate change. This objectionable impact considers severe and urgent environmental problems in the world. In Uzbekistan more than 120 million tons carbon dioxide is emitted per year on an industrial scale. Process emissions from cement production was 1.45 ± 0.20 Gt in 2016, which is around 4% of the total amount of CO_2 generated from fossil fuels. This study presents a description of the CO_2 removal process of cement manufacturing plant with a capacity of 1.2 million tons/year. Carbon capture by mineral carbonation is a technology that can potentially sequester billions of tons of carbon dioxide. Mineral carbonation is defined as the reaction of metal oxide bearing materials with CO_2 to form insoluble carbonates. CO_2 can be captured by absorbing into NaOH aqueous solutions. In addition, the CO_2 absorption capacity of NaOH solution is higher than that of mono-ethanol-amine (MEA). The theoretical amount of MEA and NaOH to capture a ton of CO_2 is 1.39 and 0.9 tons, respectively. As well as, NaOH is even more abundant, cheaper and more familiar than MEA. It is possible to obtain a solution of NaOH by water treatment of unfit salty water. In Uzbekistan, more than 50% of water is unfit for drinking. Since most of them are salt water, the problems of salt water treatment are also studied together. This generalized process is conventionally called the integrated carbon capture / water treatment processes (CC/WT). Since many cement production plants are located near unit water bodies, totally researching this integrated process may yield the expected result. In the carbon capture process, the carbon dioxide is absorbed into the sodium hydroxide solution and the solution is carbonated with gaseous carbon dioxide. After carbonation of caustic soda, a solution of sodium carbonate is obtained. Sodium carbonate resulted is crystallized in order to obtain sodium decahydrate. The main issue in the post combustion chemical absorption technologies is the large amount of energy requirements in the solvent desorption. In this case, the reduction of operating cost is important to implement for the removal process in cement industry. Therefore, instead of solvent regeneration, reaction product in the absorption column can be used as a raw material of soda ash.

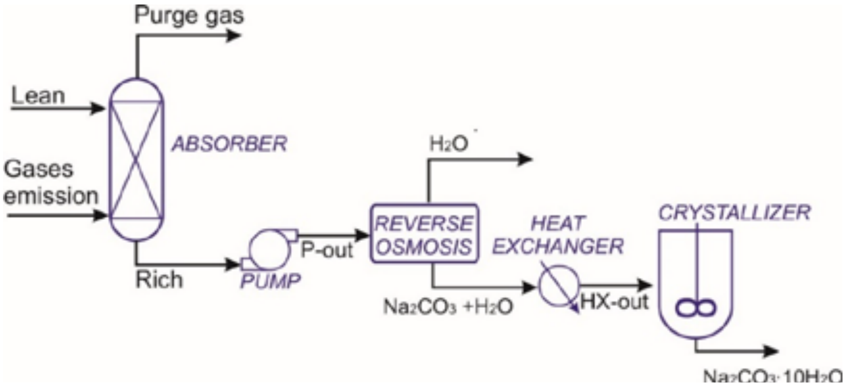

Fig. 1. Process flow diagram of carbon mineralization unit of integrated CC/WT processes

Flue gas data and process development parameters related to the cement industry, are taken from the references. The process flow diagram is developed to capture more than 95% of CO_2 from the cement industry. Absorber and crystallizer are considered as the main two-unit operation blocks in the capture and mineralization process.

Sustainable environmental technologies for the energy recovery from wastewater streams

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The shift to low-emissions decentralized renewable power sources with little water needs will be decisive in reaching a sustainable water and energy supply portfolio. Reverse electrodialysis (RED), an emerging electrochemical technology that uses ion-selective membranes to directly draw electricity out from salinity differences between two solutions, i.e., salinity gradient energy (SGE), could be a clean and steady renewable source to power the water sector from the embedded energy of waste streams. Past research has validated RED-based electricity from desalination concentrates or treated wastewater effluents [1], but full-scale RED progress still requires more techno-economic and environmental assessments that consider full process design and operational decision space from module-to system-level.

My research seeks to develop a modelling tool to provide decision-making support for early-stage applied research and to extract design and operation guidelines for full-scale RED implementation in real scenarios. We have defined, validated, and update a predictive model of the RED stack to determine the most relevant working conditions and design parameters affecting RED performance [1]. Then, we used this model to quantify the environmental loads of a lab-scale and an up-scaled RED stack under the life cycle assessment framework. From an environmental standpoint and backed by economies of scale, findings revealed RED was competitive with other renewables as solar photovoltaic or wind [2]. We also assessed the retrofit of medium-to-large-sized seawater reverse osmosis desalination plants across the globe with a RED-based energy recovery system. If all SGE were harnessed, RED could supply ~40% of total desalination plants' energy demand almost in all locations, yet energy conversion losses and untapped SGE decline it to ~10% [3]. These results denote there is a gap to bridge between the thermodynamic limit and the actual energy the RED system produces. Several variables affect the RED process, adding complexity to define optimal system designs by conventional trial and error evaluations. Hence, we are working on an optimization model formulated as a Generalized Disjunctive Programming problem to define the cost-optimal RED process design for different deployment scenarios. Preliminary results showcase mathematical programming techniques as an efficient and systematic decision-making approach over simulation alone.

Funding/Acknowledgements

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The effect of the flow and flue gas composition for the continuous electrocatalytic reduction of CO2 to formate

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The electroreduction of carbon dioxide (CO_2) is considered a promising strategy to obtain value-added products from carbon capture plants. In this sense, formic acid and formate are interesting products since they could be used not only as raw materials in various industries but also as reactants in low-temperature fuel cells and hydrogen carrier molecules. Despite a lot of great efforts that have been carried out in this field using catalysts of different nature and in different electrode configurations, the effects of other compounds in the feed gas and the flow rate are scarcely covered in the literature [1]. In this context, the main goal of this communication is to study the figures of merit in the continuous CO_2 electroreduction process at different feed gas conditions. For this purpose, the experiments were carried out working with the same experimental setup and operating conditions as previous tests developed in the DePRO research groups in order to carry out a rigorous comparative analysis with previous results [2].

Firstly, the effect of the CO_2 flow rate, as gas feed to the electrochemical reactor, was analyzed. For this purpose, different experiments varying the CO_2 flow rate in a range of 50 $mL·min^{-1}$ to 400 $mL·min^{-1}$ were carried out. The results obtained show a maximum formate concentration of 2.1 $g·L^{-1}$ and a Faradaic Efficiency of 95.6 % working with a flow rate of 150 $mL·min^{-1}$. For a second assessment, nitrogen (N_2) was introduced in the gaseous input stream to the electrochemical reactor, as well as CO_2, to study the effect of this compound for the electrocatalytic reduction of CO_2 to formate. In this sense, when the concentration of CO_2 in the feed stream is lower than 50 %, the production of formate is close to zero. However, operating with a CO_2 concentration in the input stream higher than 75 %, the figures of merit obtained in the process (i.e. formate concentration, Faradaic Efficiency, rate, and energy consumption) are very similar in comparison with employing a CO_2 pure feed.

Although the results obtained in this study are promising, further research is needed to collect more data about the effect of potential contaminants from flue gas emissions of principal fossil fuels for the future scale-up of this electrochemical process and the integration with CO_2 capture processes.

Funding/Acknowledgements
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Continuous electrochemical valorization of CO_2 to formate: assessment of the best operating conditions using NiO-based anodes in a filter press reactor

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The production of formate ($HCOO^-$) by carbon dioxide (CO_2) electrochemical reduction represents one of the most promising CO_2 utilization strategies, allowing the storage of renewable and intermittent excess energy in the form of chemicals. In this sense, previous studies carried out in the DePRO research group have focused on the CO_2 electroreduction to $HCOO^-$ process by employing different Sn and Bi-based materials in different forms of cathode configurations [1]. However, all these studies have implemented a commercial DSA/O_2 (based on Platinum and Iridium materials) as an anode to carry out the oxygen evolution reaction (OER). The high cost of these catalyst materials means that efforts are needed to develop new, cheaper and more abundant materials like Ni-based materials for future industrial scale-up. In this context, this communication focuses on studying the best operation conditions for the continuous electroreduction process of CO_2 to $HCOO^-$ in a filter-press reactor with carbon-supported Bi catalysts at the cathode and at the same time, using anodes prepared with NiO nanoparticles to carry out the OER. Promising performances were obtained by employing electrodes with NiO catalyst loadings of 0.75 $mg \cdot cm^{-2}$, since the results achieved were similar to those obtained previously with DSA/O_2. Working with the same experimental setup and identical operating conditions (current density of 90 $mA \cdot cm^{-2}$ and a catholyte flow rate per geometric area of 0.15 $mL \cdot min^{-1} \cdot cm^{-2}$), $HCOO^-$ concentrations, Faradaic efficiencies, production rates and energy consumptions of 5.5 $g \cdot L^{-1}$, 65.24 %, 3.04 $mmol \cdot m^{-2} \cdot s^{-1}$ and 335 $kWh \cdot kmol^{-1}$, respectively, have been achieved. Moreover, increasing NiO catalyst load to 1.5 $mg \cdot cm^{-2}$ under the same current density and catholyte flow and optimizing the anolyte flow rate per geometric area, it was possible to further improve process performance: $HCOO^-$ concentrations, Faradaic efficiencies, production rates and energy consumptions of 8.65 $g \cdot L^{-1}$, 100 %, 4.81 $mmol \cdot m^{-2} \cdot s^{-1}$ and 198.9 $kWh \cdot kmol^{-1}$, respectively, were achieved. Finally, the stability of the anode was also improved by changing the ionomer used for the preparation of the catalytic layer, keeping all the figures of merit at remarkable values. According to the results obtained, Ni-based materials could be considered as interesting candidates to carry out the OER for the continuous CO_2 electrochemical processes, achieving promising results compared to commercial DSA/O_2 [2].

Funding/Acknowledgements

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Zeolite-TiO_2 composite membrane for decomposition of organic matter in water

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Secured access to clean water is one of the targets in the Sustainable Development Goals (SDGs). The type of substances in waste water has been significantly increased today. Some of the pollutants are difficult to treat but harmful even at low concentrations. Applying photo-catalysis using semiconductors is an alternative water treatment technology to conventional treatments such as activated sludge process and catalytic wet air oxidation (CWAO). Photo-catalysis works under mild conditions and does not require additional chemicals. If catalysts are fixed on a membrane, a separation unit is not needed to remove catalyst powder after treating the water.

The concept of a catalytic membrane reactor (CMR) is shown in Fig. 1. The CMR morphology facilitates the supply of oxygen to the reaction field, which enhances the oxidation of organic substances in water. Pt-CMR was reported to be economically competitive in treating wastewater from dyeing factories containing e.g. formic acid [1]. On the other hand, phenol decomposition was slow [2], and it is necessary to develop new CMRs.

Recently, zeolite containing TiO_2 powder is reported to decompose dissolved organics under visible light [3]. In this study, we investigated TiO_2-zeolite composite membranes. First, the synthesis conditions of the composite material were investigated. The catalytic ability of the composite materials was evaluated using an aqueous solution of methylene blue (MB) and formic acid. The composite powder and membranes adsorbed MB, for the zeolite has affinity to MB, and decomposed MB by the TiO_2 incorporated to the zeolite.

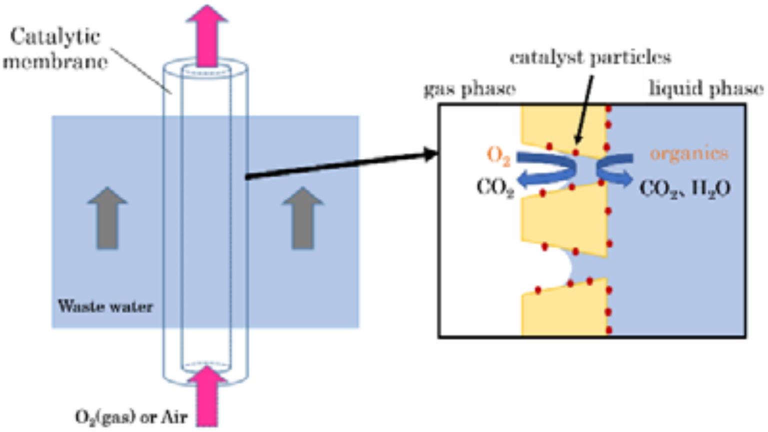

Fig. 1. Schematic of CMR.

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Kinetic study of elimination of toxic organophosphate compounds in water with MOF-808

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Organophosphorus compounds are used as pesticides in agriculture and are part of the CWA chemical warfare agents, in particular, the so-called nerve agents sarin gas (GB) and VX, belong to this family. The nerve agents are highly toxic due to irreversible binding to the enzyme acetylcholinesterase, which causes an uncontrolled increase in acetylcholine activity, leading to muscle spasms that can cause death.

The immediate reaction to a chemical incident is to evacuate people from the contaminated area; but at the same time, decontamination of the area, i.e. equipment, personnel, vehicles, etc is required as soon as possible, particularly in urban environments. This highlights the need for mobile, reliable and simple to use decontamination solutions. It is clear that chemistry, materials science and chemical engineering are required in the design of an effective CWA decontamination system. Multiple studies have been performed with the family of Zr containing MOFs (Metal Organic Frameworks), with strong Lewis acidity of the Zr(IV) node. The Zr-MOFs tested for detoxification of CWAs can be categorized into three types based on the connectivity of the Zr6 nodes (or secondary building units SBU) [1], being MOF-808 with 6 connected ligands the most reactive.

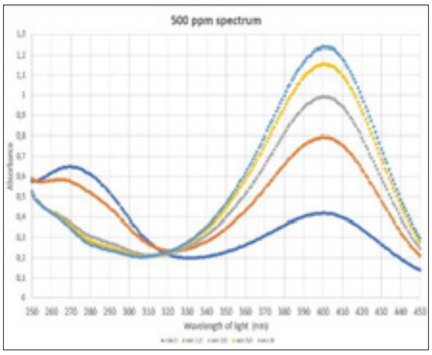

Fig. 1. Spectrum for a concentration of 500 ppm DMNP.

Due to the toxicity of CWAs, comparatively innocuous and readily available molecules called simulants are often used. The pesticide methyl paraoxon (DMNP), shows a hydrolysis mechanism similar to GB and VX and is the compound commonly used in experiments. The goal of this work is to analyze the kinetics for the degradation of DMNP catalyzed by MOF-808. A solution of 1290 mg/L was prepared with a certain amount of MOF 808 powder dispersed in N-ethylmorpholine aqueous buffer solution (0.15 M), room temperature, and sonicated for 5 minutes. After that, different amount of DMNP was added into the mixture under stirring. To monitor the progress of DMNP degradation, aliquots of different volumes was taken from the reaction solution at different time interval, diluted in N-ethylmorpholine aqueous buffer (0.15 M) and measured by UV–vis spectroscopy measurement, see Fig. 1. Finally, assuming first-order reaction kinetics, the multivariable adjustment of the different DMNP concentrations was used to calculate the kinetic parameters.

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Efficient photocatalytic degradation of the herbicide S-metolachlor with TiO_2/Fe_3O_4/rGO-5 composites

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The current increase in world population is directly related to the increase in agricultural development, water consumption, and water scarcity. To fulfill food production, a high use of herbicides, such as S-metolachlor (MTLC) is being experienced in worldwide crops finishing in water bodies [1]. Water reclamation and reuse are essential to satisfy the increasing water demand, and, here, heterogeneous photocatalysis runs as one promising and clean alternative [2]. This work aims to assess the efficiency of S-metolachlor degradation using a new composite photocatalyst made of titanium dioxide, magnetite, and reduced graphene oxide.

The synthesis of the composite, TiO_2/Fe_3O_4/rGO-5, (45/45/5 % w.w.) was carried out following a hydrothermal method. Experiments were performed in a photoreactor provided with UV-A LED technology from APRIA SYSTEMS with a maximum irradiance of 200 W/m^2. Initial MTLC and catalyst concentrations were 0.11 mM and 0.5 g/L, respectively. MTLC concentration was measured by High Performance Liquid Chromatography. A comparative analysis of the ternary composite to TiO_2/rGO-5 and bare TiO_2 P25 is shown in Fig. 1a. Adsorption equilibrium was reached in less than 30 min. Then, UV-A light was turned on and after 30 minutes 98 % of MTLC was removed. Fig. 1b shows that mineralization was slower than MTLC removal, and acetic and formic acid were detected in the last minutes' samples. Nevertheless, it was possible to confirm that the remaining compounds were chlorine free, because all chlorine from MTLC was released to the aqueous medium.

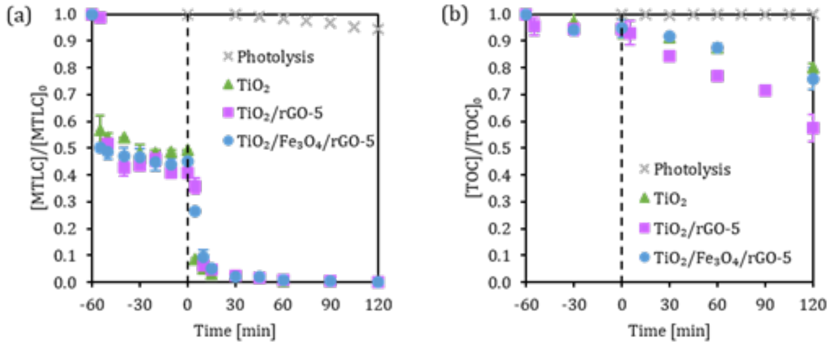

Fig. 1. (a) MTLC removal, and (b) mineralization expressed as dimensionless Total Organic Carbon (TOC) using different photocatalysts irradiated with UV-A source at 365 nm.

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PCDD/Fs formation during Triclosan oxidation: Electrochemical oxidation vs. photocatalysis

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Introduction

Triclosan (TCS) –antimicrobial and antifungal compound present in many daily care products– is an emerging contaminant with a high resistance to biodegradation. Advanced Oxidation Processes (AOPs) are applied to eliminate this compound from aqueous matrices, but, the formation of more hazardous by-products such as dioxins and furans (PCDD/Fs) can occur. In this work, electrochemical oxidation (ELOX) and photocatalysis (PC) have been studied and the PCDD/Fs produced were analyzed. Finally, toxicity expressed as Toxic Equivalents (TEQ) of TCS degradation with both technologies has been evaluated [1].

Materials and Methods

In all cases, 10 mg/L of TCS were employed. ELOX experiments were carried out in a laboratory cell system, whereas PC experiments were conducted in laboratory-scale plant with UVA-LED irradiation. NaCl and Na_2SO_4 were used as electrolytes, and TiO_2 was employed as catalyst (0.75, 1 and 1.5 g/L). PCDD/Fs were analyzed and quantified in HRGC-HRMS by the SERCROM of the University of Cantabria.

Results

In ELOX, complete TCS degradation was achieved for both electrolytes. Total PCDD/Fs concentration achieved values up to 411 pg/L when NaCl was used. TEQ increased 11 and 10 times in comparison to the untreated sample for NaCl and Na_2SO_4, respectively. When applying PC, TCS has completely eliminated, and total PCDD/Fs increased 4300, 5200 and 42 times for 0.75, 1 and 1.5 g/L of TiO_2 respectively; but TEQ values increased 63, 42.3 and 6 times for 0.75, 1 and 1.5 g/L of TiO_2, respectively. The best conditions of TCS degradation in terms of TEQ were achieved using PC with 1.5 g/L of TiO_2 (0.61 pg/L of TEQ). In general, in ELOX experiments when employing Na_2SO_4, less TEQ values were obtained versus NaCl. In the case of PC, the higher the TiO_2 loading, the lower TEQ values. Thus, the appropriate selection of the remediation treatment and the operating conditions are crucial to apply sustainable technology for the emerging pollutants elimination.

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Qualitative morphology prediction of polymeric membranes

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Polymeric membranes synthesized by non-solvent induced phase separation are widely used in multiple applications. Depending on the application different morphologies are required. The synthesis methodology uses a trial-and-error procedure based on previous experience and literature, which is expensive and time consuming [1]. The development of a suitable mathematical model could result in reliable predictions of the membrane morphology before its fabrication, saving laboratory time and money. In this work, a mathematical model that includes thermodynamic and kinetic phenomena of phase separation process is presented for ternary polymeric systems. The thermodynamic of a ternary polymeric system is depicted by a ternary phase diagram (Fig. 1), where the binodal curve represents the equilibrium boundary between the homogeneous phase and the heterogeneous phase. When the precipitation pathway crosses the binodal curve, the solution separates into two phases. The thermodynamic model was developed applying Flory-Huggins theory and ternary interaction parameters to fit the curves [1]. The kinetic model was based on Fick's law as present in the literature [2]. An important novelty consisted of integrating thermodynamic aspects into the kinetic model. The movement of the diffusion layer is driven by the thermodynamic equilibrium. An advanced methodology of image processing by Matlab, allowed the analysis of scanning electron microscopy (SEM) images to get a qualitative validation of the model by comparing the simulated and experimental membrane porous profile. Two systems PVDF/NMP/Water and PCL/NMP/IPA with instantaneous and delayed demixing, respectively, were studied

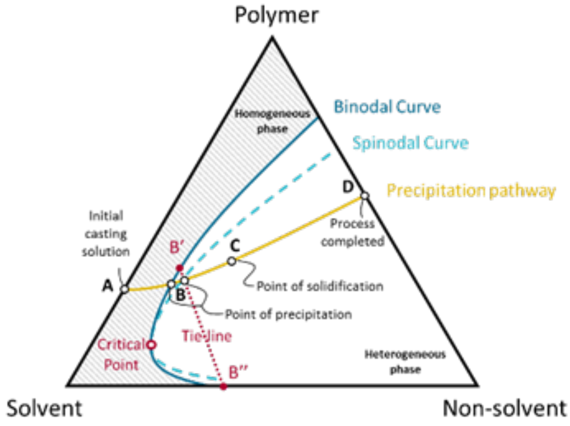

Fig. 1. Ternary phase diagram

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Influence of drying conditions on the dehydration performance of zeolite membranes

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The Paris Agreement, adopted in 2015 is an international treaty that regards the realization of a low-carbon society as an urgent issue. In addition to energy saving of processes, it is necessary to shift to use renewable energy. Even though the usage of fossil fuel needs to be decreased, we still need to rely certain part on the fossil fuel. Accordingly, carbon dioxide separation methods and efficient usages of separated carbon dioxide are required.

An example of carbon dioxide usage is the synthesis of methanol with hydrogen obtained from carbon dioxide and renewable energy:

$$CO_2 + 3H_2 \rightleftharpoons CH_3\,OH + H_2O \qquad \text{(Eq.1)}$$

This reaction is an equilibrium limited reaction. If water is removed from the reaction field using a membrane, the conversion rate increases [1]. Membrane must be sufficiently stable against heat and water vapor to apply above reaction.

In this study, two types of zeolite membranes, A-type and MOR-type, were compared. Membranes were heated in dry gas and in wet gas at 150 to 200 °C. Then, the membranes were analyzed with dehydration performance using an ethanol solution. Table 1 shows some results. The water selectivity of A-type membrane decreased after heating at 150 °C in dry conditions. The selectivity partially recovered by immersing the membrane in water. On the contrary, heating A-type membrane in vapor did not change the selectivity. Same tendency was observed with MOR-type membranes. Surface silanol groups may be condensed in dry heating and made the membrane less hydrophilic [2]. Results showed that membrane reactor is necessary to be heated in the presence of water vapor.

Table 1. Zeolite membrane performance evaluation
(PV: 90wt% Ethanol/10wt% H_2O as feed)

Membrane type	Treatment conditions	H_2O concentration in the permeate (wt%)	Selectivity (-)	Flux (kg・m^{-2}・h^{-1})
A-type membrane (1)	80 C dry	99.1	1145	2.0
	150C dry	83.6	61	1.9
	Water immersion	92.6	151	1.5
A-type membrane (2)	80 C dry	99.0	1196	1.8
	150C in H_2O vapor	99.3	1619	1.5
MOR-type membrane	80 C dry	99.7	2941	1.0
	150C in H_2O vapor	99.6	2240	1.0

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The role of Anion Exchange Membranes for CO_2 electroreduction in alkaline media

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Electrochemical reduction of CO_2 (CO_2RR) is a promising technology for coupling CO_2 conversion into value added products and energy storage from renewable sources. Mass transport limitations in electrochemical cell reactors are noticed as one of the mayor challenges, due to the poor solubility of CO_2 in aqueous electrolytes. In this regard, polyelectrolyte membrane reactors (PEMER) are gaining relevance, because they allow the elimination of the liquid electrolytes. Thus, the study of the role of the ion exchange membrane (IEM) is an important issue in the electrochemical reactor configuration, as they provide the ionic media in which the reaction takes place, controlling the pH and facilitating ion transport (and hindering product crossover) between the electrodes. In particular, alkaline media present several advantages by reducing the competition of Hydrogen Evolution Reaction (HER) compared to acid media, lower ohmmic losses than neutral and a high concentration of hydroxide anions in the surroundings of the catalyst to improve the kinetics of the CO_2RR, favoring the formation of C_2 products [1].

In this work, we studied the behavior of two commercial alkaline anion exchange membranes (AAEM) suitable for the construction of a PEMER for CO2RR: Sustainion and FAA-3. Furthermore, we have introduced the utilization of biopolymer chitosan (CS) as binder in the preparation of Cu-based electrodes Gas Diffusion electrodes (GDEs) and also as overlayer of the electrodes, creating a novel configuration of Membrane Coated Electrodes (MCEs) [2]. The results obtained shown that chitosan is a promising alternative as green binder, since the results for C_2H_4 production were improved with the Cu:CS GDE compared to those with commercial ionomers as binders, both in terms of Faraday Efficiency (FE) and productivity. Also, one of the MCEs tested reached a FE of 98 % for C_2H_4 at 10 mA/cm^2 in a continuous filter press cell, with a total cell potential of 3 V. Further studies should consider the reduction of the membrane overlayer thickness of this MCEs (currently 50 µm) to reduce the ohmmic losses and consequent overpotentials.

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Utilization of Geothermal Water in Industry as Process Water After Membrane Desalination

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In this study, the usability of the geothermal water taken from the reinjection line of the geothermal heating center as process water for various industries was investigated. For that purpose, a pilot scale membrane desalination system containing nanofiltration (NF) and reverse osmosis (RO) membranes was installed at a geothermal heating center in Izmir. Field tests were conducted using spiral-wound NF (Toray-NF8040-70) and RO membranes (Toray-TM720D-400) on the pilot-scale membrane test system. The effect of applied pressure on the performance of membranes to desalinate geothermal water was investigated. The quality of product water obtained by NF and RO membranes were compared with process water quality requirements by different industries. According to the results obtained, the desalinated water can be used as cooling water and process water for steam generation, paper, and textile industries [1,2].

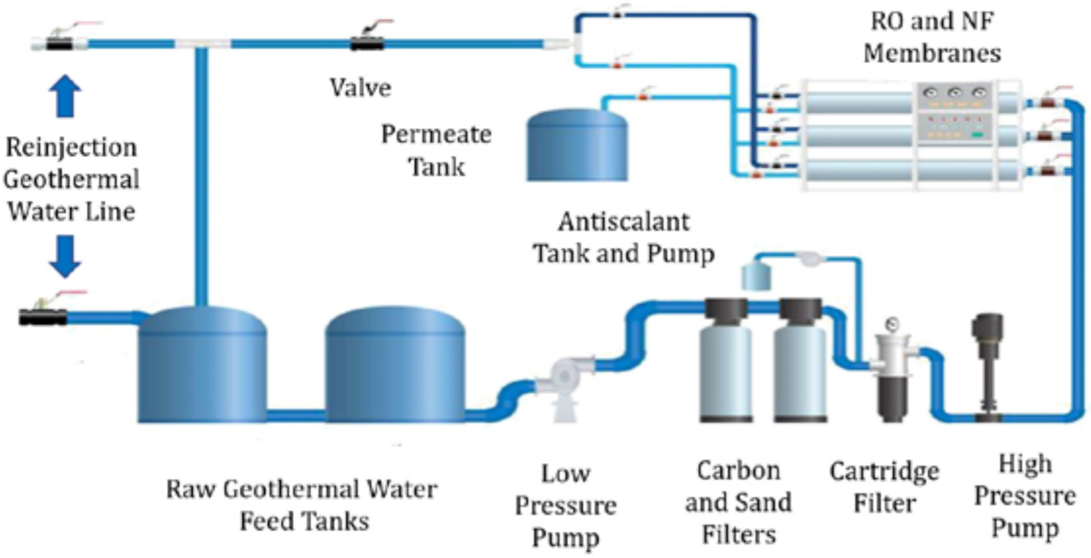

Fig. 1. The flow diagram of the large-scale NF/RO pilot system

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This symposium, originally founded in 2013 by Universidade Nova de Lisboa, Universidad de Zaragoza and University of Yamaguchi, is conceived as an international forum for the dissemination and reinforcement of research collaboration among the participating institutions. Different institutions have been invited to participate in subsequent editions. University of Cantabria had the opportunity to participate in the 2nd and 5th edition, and we are honoured to organize the present 6th conference, that unfortunately, was forced to be celebrated remotely due to the COVID-19 global pandemic.

This edition continues with the topics discussed in the previous symposium. Scientific topics are aligned with the 2030 Agenda for Sustainable Development, and aimed at the study of key-enabling technologies and processes to ensure a sustainable industry for the society of the future.

As a novelty in this edition, the symposium will consist of two events that will take place in parallel:

- Live online scientific seminars given by reputed experts in the field of Chemical Engineering and related complementary scientific areas.
- Students workshop aimed at the dissemination of the research activities of PhD and MS candidates.

A special seminar session has been included, devoted to the dissemination of research goals and collaborative outcomes of the X-MEM project (5th EIG-Concert Japan joint call on «Porous structured materials»), with a partnership composed of researchers from University of Cantabria (Spain), University of Yamaguchi (Japan), Atilim University (Turkey), Ege University (Turkey), Hacettepe University (Turkey) and Jerzy Haber Institute of Catalysis and Surface Chemistry (Poland).

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