3rd Workshop

of the Excellence Network on Environmental and Energy Applications of the Electrochemical Technology

SUSTAINABLE ELECTROCHEMICAL TECHNOLOGY

14-15 May 2019

Toledo, Spain

BOOK OF ABSTRACTS

Aplicaciones Medioambientales y
Energéticas de la Tecnología
Electroquímica

E3TECH

Program of the

3rd Workshop
of the
Excellence Network
on Environmental and Energy Applications of the Electrochemical Technology

Sustainable Electrochemical Technology

14-15 May 2019

Toledo, Spain

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Session 1. Tuesday 14 May 2019

Schedule	Authors	Communication
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14:30-14:40 h	*L. Cañizares, M. A. Khan, M. Massaros (ARVIA TECHNOLOGY LTD.)*	Arvia Technology Ltd. New approach of Advanced Oxidation Process
14:40-14:50 h	*L. Meda (ENI)*	The interest of an oil & gas company towards energy storage
14:50-15:00 h	*P. Camprovin, J. Manzano, M. Arnaldos, Y. Aguilera, J. Suescun (CETaqua – SUEZ Group)*	EQTECH technology: evaluation of full-scale implementation results in prioritized industrial sectors
15:00-15-10 h	*Y. Asensio, P. Zamora, M. Stiven Romero, Á. Encinas, X. Tomas, P. Icarán, V. Monsalvo, F. Rogalla (AQUALIA)*	AQUALIA and Bioelectrochemical Systems (BES). Lessons learnt and future prospects for the development of high-efficient innovative bioelectrochemical technologies
15:10- 15:40 h	**ROUND TABLE**	
PUBLIC ENTITIES		
15:40-15:55 h	*F. Orts, A.I. del Río, J. Bonastre, F. Cases*	Effect of the presence of chloride in the electrochemical treatment of industrial textile wastewater. Trichromy Procion HEXL®.
15:55-16:10 h	*M. P. Fei, A. Galia, F. Vicari, O. Scialdone*	Electrochemical treatment of wastewater with different conductivities
16:10-16:25 h	*E. Pastor*	Electrocatalysis on graphene-based Materials
16:25-16:40 h	*F. Santos, J. Abad, A. Urbina, A.J. Fernández Romero*	Environmental and economical requirements for a sustainable Zn/air battery
17:00 h	**E3TECH MEETING**	

Arvia Technology Ltd. New approach of Advanced Oxidation Process

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Arvia Technology is water/wastewater treatment company, composed of around forty multidisciplinary employees from around all over the world. It is based on Runcorn, Cheshire, United Kingdom.

Arvia Technology is globally active, and it is experiencing a rapid expansion in the last few years on emerging economies such as China and around Europe and USA. Arvia Technology is focus on the following markets: pharmaceutical, oil and gas, food and beverage, chemical, utilities and drinking water.

Arvia Technology have developed a new approach of Advanced Oxidation Process (AOP) in which two technologies are combined into a single reactor: adsorption and electrochemical oxidation/regeneration. The first one, concentrates the organics onto an adsorbent surface, while electrochemical oxidation mineralizes the organics to CO_2, as well as, regenerates the adsorbent continuously and simultaneously, please see Figure 1.

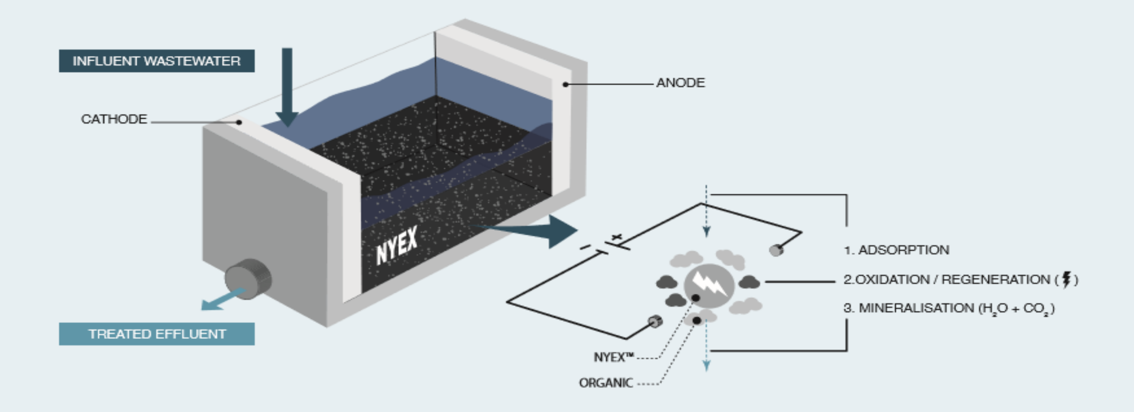

Figure 1. Schematic of the Nyex™ System

It is well known that AOPs are controlled (limited) by mass transfer as well as require a minimum conductivity of the water/wastewater to ensure the pass of the electrical current through the cell by resulting into a low operational cost. Consequently, the key component of the process is the adsorbent material, property of Arvia Technology Ltd., which has been developed under the trade name of Nyex™. This material is a highly electrically conductive carbon-based material. Because of the Nyex™ is highly conductive it can be used as three-dimensional electrode within an electrochemical cell with the applying of electric current through the system. The adsorbent eliminates the disadvantages mentioned earlier by also acting as a conducting bridge to reduce or eliminate the need for electrolyte in low conductivity wastewater solutions. This therefore results in a reduction in the cell voltage, and consequently the operating cost.

Adsorption processes are very good at achieving low discharge consent. However, it is purely a concentration process. Once the adsorbent is spent then it must be disposed of, incinerated or regenerated. In this regard, regeneration of the adsorbent has the benefit of destroying the organics and restore the adsorptive capacity of the adsorbent. This can be achieved on site at room temperatures and pressures.

In addition, Arvia has developed another version of the technology. The construction materials of this reactor allow to work with current densities one magnitude order higher than the conventional system above mentioned. The range of current density is from 12.5-25 mA/cm^2.

The interest of an oil&gas Company towards energy storage

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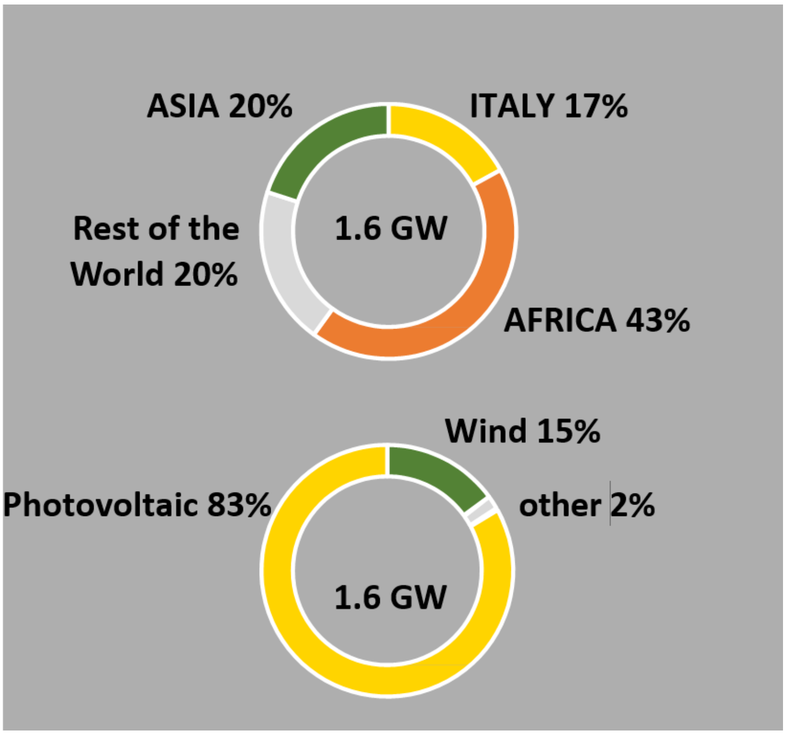
ENI is an Italian company mainly devoted to oil & gas business. ENI operates in 70 Countries with about 35.000 employees, with a great organization ability. In parallel to the main business areas, since about twelve years ago the Company decided to build a new Division devoted to Renewable Energies and Environmental projects, starting from research activities and now going towards concrete deployment projects. A strategy for real de-carbonation has declared in the last five years: new technologies are searched to improve energy efficiency; to decrease carbon impact; to save emissions; to clean polluted areas; to forest withered areas.

In the recently presented business plan, ENI claimed an investment in renewable energy generation of 1.4 bln € to be spent in three years during 2019-2022. This translates in an installed capacity of 1.6 GW, mainly in photovoltaic installations (83%), windmills (15%) and others (2%). For the installation of these plants ENI will operate in different part of the world, where the company is already active in exploration and production: Africa (43%), Asia (20%), Italy (17%) and other Countries (20%).

Renewable sources available today (PV and wind) ask for a combination with energy storage systems due to their intermittence nature. To answer to daily and weekly energy storage the electrochemical technologies give a wide panorama of answers. The main interest of the company is towards stationary storage, with large energy amounts and relatively moderate power, low cost per kWh, and long duration. For that it is necessary to study systems standing beyond Li-ion batteries.



EQTECH technology: evaluation of full-scale implementation results in prioritized industrial sectors

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Electrochemical processes are new ways of meeting the environmental requirements in terms of pollutant removal from wastewater and energy savings. Until now, they have not been employed very often at large scale mainly due to their high investment costs and the fast erosion of the first generations of electrodes. But during the recent years, many studies have been conducted in this field, and new materials have been employed to manufacture more robust components. Besides, the possibilities offered of energy savings and production of valuable products make these processes more economically attractive. These are the reasons why they are more and more employed to treat harsh waters where cost of disposal and treatment is usually expensive. They are presented as alternatives to conventional treatments in order to treat efficiently the liquid wastes before discharge.

SUEZ has a patented electrochemical technology, EQTECH, able to treat a wide nature of the contaminants from different complex industrial effluents. The technology combines different electrochemical processes such as electrocoagulation (EC), electro-peroxicoagulation (EP) and electro- oxidation (EO), reaching a high efficiency in the removal of contaminants. Other processes such as membrane treatments or dissolved air flotation are combined with the electrochemical systems to separate the sludge generated and maximize the efficiency of the treatment. Currently, SUEZ has five (5) references in operation: one (1) in pharmaceutical industry, two (2) in chemical industry and (2) two additional in automotive sector. Additionally, SUEZ is gaining experience in other relevant sectors like Oil and Gas and mining sectors.

Before to continue with expansion of their EQTECH technology, SUEZ launched a project in order to audit current on-going facilities with special focus on EPC and EO. Main objective was to evaluate real effective technology performance and risk and allowing providing the right level of confidence on that. Audits were carried out in three out of five sites, one of each sector, pharmaceutical, chemical and automotive. Technology implemented was EP in first two sites and EC in the last one, showing satisfactory results in removal of COD of 47% and 56%, and allowing improvement of BOD-to-COD ratio in case of EP (chemical and pharmaceutical sectors) and in case of automotive reducing metals: Ni, Zn, Cr and Cu in 98-99%. Measured consumption was 3.6 $€\cdot m^{-3}$, 2,97 $€\cdot m^{-3}$ and 1,1 $€\cdot m^{-3}$ for pharmaceutical, chemical and automotive industry respectively in range with the initially specified in the design. The results allow consolidating the technology EQTECH as an interesting solution for detected niche markets and allow continuous promotion of new developments in this field, either internal or in collaboration with external partners.

Acknowledgements

The project was internally funded by SUEZ Global, as a strategic technology to address specific markets.

AQUALIA and Bioelectrochemical Systems (BES). Lessons learnt and future prospects for the development of high-efficient innovative bioelectrochemical technologies.

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Wastewater treatment is a process that converts wastewater into an effluent that can be either returned to the water cycle with minimal environmental issues. The current technologies for this purpose are quite old and normally characterized by energy-intensive and chemical consuming systems (chemical coagulation, aerated treatments, etc.) leading to unsustainable and poor efficient performance of wastewater treatment and desalination plants. Against this background, the development of innovative high-efficient technologies committed to the environment and to the circular economy principles, as the bioelectrochemical systems (BES), turns mandatory.

A hotly debated topic lies around the up scaling and technical and economic feasibility of BES for their application at large scale. During the last years, the Innovation and Technology Department of AQUALIA have pursued the up scaling and field implementation of BES-based processes through the execution of several projects. Along with the technical and scientific development, the relationship cost- benefit has been thoroughly assessed towards a future implementation at industrial scale. In summary, the above-mentioned projects and main goals are listed below:

1. Develop sustainable desalination technologies. Project **H2020-MIDES** (www.midesh2020.eu), aims to revolutionize desalination by developing a low-energy sustainable process called Microbial Desalination Cell (MDC; EP3336064A1). The integration of MDC technology with commercial reverse osmosis allows seawater desalination with an energy consumption below 0.5 kWh/m^3 due to the energy recovered contained in the wastewater.
2. Maximize the recovery of nutrients and energy from wastewater. Project **LIFE-ANSWER** (www.life-answer.eu), where a combination of electrochemical technologies, electrocoagulation and MEC technology, continuously treat wastewater from a brewery industry. Recycle aluminum is used as anode during electrocoagulation, while the bioelectrochemical reactor (EP14382131.2) is electro-stimulated achieving high COD consumptions and producing an enriched biogas (methane and hydrogen) with a high-energy content. This combination of technologies renders a low-energy consumption and delivers a high-quality effluent that is further reused after a membrane post-treatment.
3. Promote the conversion of waste to high-added value compounds with bioelectrochemical reactors. Project **SMART GREEN GAS** and **H2020-SCALIBUR** (www.scalibur.eu), by the development of a high-efficient bioelectrochemical reactors (for the production of methane (bioelectro-methanisation on the surface of the cathode material) and alcohols from the carbon dioxide produced during the anaerobic digestion step in WWTP.
4. The wastewater treatment of highly polluted wastewaters. Project **FEDER INTERCONECTA-ADVISOR**. A bioelectro-stimulated reactor will be operated for the wastewater treatment of a highly polluted stream from slaughterhouses. An enriched biogas is produced that is further treated by an upgrading process for the continuous generation of bio methane (<95%) for its use as vehicular fuel (ABAD® technology).

The commitment of AQUALIA with disruptive and out-of-the box approaches based on the upscaling and further industrial implementation of microbial electrochemical technologies is supported by CAPEX and OPEX analysis where not only the technical, but also the economic feasibility are demonstrated.

Acknowledgments: These works have been founded by European H2020 research and innovation programs: SCALIBUR (G.A 817780), MIDES (G.A 685793). European LIFE programs: ANSWER (LIFE15/ENV/ES/000591). Finally, with national program FEDER-INTERCONECTA and CIEN programs founded by CDTI (ADVISOR and SMART GREEN GAS).

Effect of the presence of chloride in the electrochemical treatment of industrial textile wastewater. Trichromy Procion HEXL®.

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The textile industry is responsible of the 20% of contaminated water in the world and it is only able to recycle 1% of the more than 25,000 million tons of textile waste that is generated each year. With the purpose of providing solutions to decrease this polluting load, our group during several years is studying the possibility of applying electrochemical techniques in the treatment of textile wastewater. Our objective has been to check the power of these techniques in the decolourization and degradation of solutions containing reactive dyes, which are one of the family of dyes most used in the textile industry.

In the present study, the electrochemical treatment of industrial textile wastewater obtained after the dyeing of cotton fabrics in the presence of chloride is studied. The dyes used in this study are bifunctional reactive azo dyes belonging to the Trichromy Proción HEXL. These dyes have in their structure two azo groups as chromophores and two monochlorotriazinic groups as reactive groups.

Electrochemical treatments by oxide-reduction at 125 mAcm^{-2} were carried out in a filter-press cell without separation of compartments using a Ti/SnO$_2$-Sb-Pt electrode as an anode and a stainless steel electrode as a cathode. This experimental procedure has been shown effective in previous experiences using sulphate as electrolyte.

The degree of degradation of the dyes is evaluated by measurements of Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and Total Nitrogen (TN), which allow us to know the Average Oxidation State (AOS), the Carbon Oxidation State (COS) and the Average Current Efficiency (ACE) throughout the electrolysis. AOS variations are related with the modifications that take place in the composition and in the toxicity/biodegradability of the sample. COS and ACE could estimate the efficiency of the process. COS provides an estimate of the efficiency with which the carbon structure of the dye molecule is degraded. The ACE value provides information on the efficiency of the degradation not only of the carbon structure but also of the functional groups containing heteroatoms.

The kinetics of decolourization and the intermediates generated have been studied through measurements of High Performance Liquid Chromatography and UV-Visible Spectrophotometry.

The results indicate that a significant decrease in TOC, COD and TN is obtained. Moreover, the process takes place efficiently and the AOS and COS data confirm the presence of stable oxidized intermediates in solution after electrolysis. The kinetics of decolourization and the UV-Visible Spectrophotometry indicates that full decolourization is obtained at a value of loaded charge of around 7 AhL^{-1}.

If the results obtained are compared with those of previous experiences in which the electrochemical treatment has been carried out using sulphate as electrolyte and in the absence of chlorides, it is concluded that the use of chlorides considerably improves the performance of the process. This is mainly due to the generation of an inorganic mediator like “active chlorine” which is a strongly oxidizing agent. However, this species is also capable of attacking the surface of the Ti/SnO$_2$-Sb-Pt electrode, increasing its electrical resistance and shortening the life service of such anode.

In spite of the latter and given the high degree of mineralization obtained and the high rate of decoloutization observed, this treatment could be a viable alternative in the purification of real textile effluents containing this type of dyes.

Acknowledgments: The authors wish to thank the Spanish Agencia Estatal de Investigación (AEI) and European Union (FEDER funds) for the financial support (contracts MAT2016-77742-C2-1-P and MAT2016-77742-C2-2-P). Financial support of Red E3TECH (CTQ2017-90659-REDT) is also acknowledged.

Electrochemical treatment of wastewater with different conductivities

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In the last years, it has been shown that electrochemical processes can be used for the effective treatment of wastewater contaminated by organic pollutants resistant to conventional biological processes and/or toxic for microorganisms [1–5]. It was shown that some electrochemical approaches, including the direct anodic oxidation at suitable anodes such as boron-doped diamond (BDD) and/or electro-Fenton (EF) at suitable operating conditions and cells [1–6] can allow to treat effectively a very large number of organic pollutants. However, these processes require the consumption of significant amounts of electric energy.

In previous works we have shown that reverse electrodialysis processes fed with water with different salinities (such as sea and river water) can be used in order to treat wastewater contaminated by both Cr(VI) and organic pollutants with no energetic inputs [7-8]. Hence, it is possible to exploit the utilization of different kinds of water with different conductivities in order to feed the reverse electrodialysis stack. In particular, it would be appealing to feed the reverse electrodialysis stack with wastewater with different conductivities. Hence, in this work we have studied the electrochemical treatment of wastewater carried out using a reverse electrodialysis stack fed with wastewater with different conductivities in order to reduce the energetic consumptions.

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Electrocatalysis on Graphene-Based Materials

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The worldwide energy demand increases and the search for energy conversion process becomes compulsory. In this context, Fuel Cell (FC) and Electrolyzer (EL) technologies emerge as attractive alternative for clean energy production and storage. Graphenic materials (GMs) offer many advantages as catalyst support and metal-free catalyst due to their high conductivity, elevated surface area and low cost. Thus, graphene oxide (GO) is usually employed as cheap precursor to obtain reduced graphene oxide (rGO). GO has low electric conductivity, due to the formation surface oxygen groups during its synthesis from graphite, which limits its use in electrochemical devices. To solve this problem a great diversity of physical and chemical methods that are widely found in the literature has been employed to produce doped-graphene with P, B, S and N elements[1]. Doping process causes an electronic modulation of the carbonaceous grid improving the electroactivity toward some reactions of interest. Dual-doped graphene exhibits excellent performances when are used as cathode for FCs and ELs[2].

In the present communication, graphene materials (GMs) were synthesized from GO, which was prepared by a modified Hummers method. Then, GO was chemically reduced by diverse methodologies to introduce in the graphenic structure functional groups and heteroatoms, as well as to support metallic nanoparticles (Ni, Mo, Co, Pt, Pd). Reactions involved in FCs (hydrogen or alcohol oxidation, oxygen reduction) as well as ELs (hydrogen and oxygen evolution) were studied (Figure 1). Physicochemical characterization was carried out by several X-ray techniques such as diffraction (XRD) and dispersive energy (EDX), Raman and infrared spectroscopies. The electrochemical performance toward benchmark reactions was carried out in a wide pH range by potentiodynamic and potentiostatic techniques coupled with rotating ring-disk electrode (RRDE) and differential electrochemical mass spectrometry (DEMS).

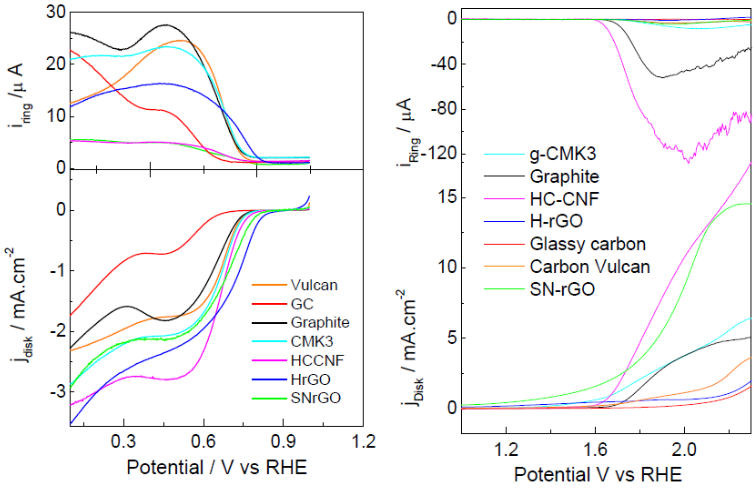

Figure 1. Polarization curves for carbon materials in 0.1 M NaOH recorded at 1600 rpm. Left: oxygen reduction reaction, 2 mV/s, E_{ring} = 1.20 V. Right: oxygen evolution reaction, 10 mV/s, E_{ring} = 0.40 V.

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Acknowledgements

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Environmental and Economical Requirements for a Sustainable Zn/air battery

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The transition towards an energy system with high penetration of renewable energy demands the use of energy storage. Batteries will be part of the solution, specially for a massive penetration of electric transport which will require small or medium batteries which are sustainable from an environmental and an economical point of view.

Lead-based, alkaline or lithium-ion based batteries are already in the market. Innovative technologies such as Li/air, with an energy density theoretically ten times higher, are being investigated; the environmental impact for its production could be reduced by an amount between 4 and 9 times when compared with conventional Li-ion and by recycling, up to 30% of production related environmental impact could potentially be avoided [1]. Nevertheless, it is difficult to compare the environmental impact of well stablished and emerging technologies since their use-phase (specially cycling and lifetime) is very different and it makes difficult to propose a functional unit for a comparative Life Cycle Assessment (LCA). We propose a methodology to evaluate the sustainability of different energy storage systems in which conventional batteries are compared with innovative approaches such as metal/air batteries, with special focus on a comparison between Li/Air and Zn/Air batteries [2]. The result of the evaluation depends mainly on the processing routes for battery fabrication, the efficiency and cyclability of the battery during the operational phase and the decommission of the battery including recycling and/or land- filling at the end of life. Using the same functional unit for the different technologies (energy stored averaged throughout battery life time), the requirements for the Zn/air battery in order to become the solution with lower environmental impacts are provided taking into consideration that electrolyte formulation, cell design and separators affects the properties of the battery.

Similarly, a calculation of the levelized cost of energy storing capacity of the battery (averaged throughout battery life time) provides an economical comparison of different technologies and poses clear requirements for any new technology in order to penetrate the market.

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Session 2. Wednesday 15 May 2019 (morning)

Schedule	Authors	Communication
11:00-11:15	*A. Puga, S. Escudero, E. Rosales, M. Pazos, M. A. Sanromán*	Removal of micropollutants from aquatic environment by two-stage approach: adsorption and electro-Fenton
11:15-11:30	*A. Soriano, D. Gorria, L. T. Biegler, A. Urtiaga*	Towards an efficient electrolysis of perfluorocarboxylic acids through integration with membrane separation using process system engineering tools
11:30-11:45	*A. Raschitor, J. Llanos, M. A. Rodrigo, P. Cañizares*	Is it worth using the electrodialysis/electro-oxidation system for the removal of pesticides? Process modelling and role of the pollutant
11:45-12:00	*R. M. Fernández-Domene, G. Roselló-Márquez, R. Sánchez-Tovar, B. Lucas-Granados, J. García-Antón*	Application of WO_3 nanostructures synthesized by anodization in the photoelectrochemical degradation of pesticides
12:00-12:15	*J. García-Cardona, I. Sirés, F. Alcaide, E. Brillas, F. Centellas, P.L. Cabot*	Properties and electrochemical performance of supported Pt(Cu) core-shell catalysts for hydrogen oxidation
12:15-12:30	*E. Castillo-Martínez, J. Carretero-González*	Sustainable electrochemical energy storage materials systems for off-grid, poor and remote communities
12:30-12:45	*J. Carrillo-Abad, J. Mora-Gómez, M. García-Gabaldón, E. Ortega, M. T. Montañés, S. Mestre, V. Pérez-Herranz*	Study of the use of new ceramic materials for the removal of norfloxacin by electro-oxidation in chloride media
12:45-13:00	*A. J. dos Santos, E. Brillas, C. A. Martínez-Huitle, I. Sirés*	Solar photoelectro-Fenton treatment of mixtures of Tartrazine, Ponceau SS and Direct Blue 71 azo dyes
LUNCH		

Removal of micropollutants from aquatic environment by two-stage approach: adsorption and Electro-Fenton

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Micropollutants refer to residue from substances, use every day in modern society, including for example pharmaceuticals and personal care products (PPCPs). They are commonly present in waters at trace concentrations. The occurrence of PPCPs in different environmental compartments has been reported increasing in the last years as a result of their growing consumption (Ebele et al 2017). This fact raises concerns about their potential adverse effects to humans and wildlife. The main source for their release to the environment is through of the effluents of the wastewater treatment plants (WWTPs) due to that these systems were not designed for the treatment of these complex substances therefore they are ineffective in their removal.

In the last years, several treatment alternatives have been effectively applied for the removal of these compounds in aquatic environment, among them Electrochemical Advance Oxidation Processes (EAOP) have shown great ability for the degradation and mineralization of PPCPs (Rosales et al 2018). However, the huge amount of wastewater, that should be treated in the WWTP, and the low concentration of these pollutants are the bottle neck for the implementation of these processes at industrial scale because the elevated operational cost associated to these advanced techniques.

In this study, a simple low-cost pretreatment stage, adsorption, is proposed for overcoming this drawback. It is expected that this initial stage reduces the volume of wastewater to be treated by the EAOP. In order to achieve this goal, two different approaches were proposed for the adsorption of the selected model pollutants (fluoxetine (FLU), sulfamethoxazole (SMX) and methyl paraben (MePa)) using different materials as adsorbents. On the one hand, the use of commercial carbon aerogels (NQ30 and NQ40) of different characteristics. On the other hand, the use of lignocellulosic wastes and the biochars, obtained after their pyrolysis. The adsorption process was studied in deep and the best adsorption capacities were reached using carbon aerogels (NQ 30 and NQ40). After that, the kinetic parameters and the adsorption isotherms were studied. For these matrixes, it was stablished a strong interaction adsorbate-adsorbent and the desorption process was difficult to accomplished using traditional solvents. Then, the direct degradation of the pollutants on the solid matrixes was carried out by Electro-Fenton treatment (EF) following our previous experience (Díez et at 2018). The reactor design and operational variables affecting the process (current intensities, electrode material, pH, solid liquid ratio, catalyst concentration, etc.) were studied and the process was optimized.
Under the best conditions, it was reached high removals of the pollutants on the adsorbents. In addition, the reutilization of the regenerated adsorbents during different cycles of adsorption-pollutant degradation process was effectively accomplished, which confirms the suitability of developed process as a viable alternative in the treatment of the selected micropollutants.

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Towards an Efficient Electrolysis of Perfluorocarboxylic Acids Through Integration with Membrane Separation using Process System Engineering Tools

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The ubiquitous presence of man-made perfluoroalkyl substances (PFASs) in the environment have led to new regulations about their use and manufacture [1]. Moreover, concentration in the environment of persistent short-chain perfluorohexanoic acid (PFHxA) is increasing due to biodegradation pathways of 6:2 fluorotelomers used as substitutes of long chain perfluoroalkyl compounds [2]. In spite of the excellent yield of BDD electrolysis in PFASs oxidation, the practical implementation of the technology is hindered by its slow overall kinetics, that results from mass transfer limitations [3].

Membrane separation is herein proposed as a way to increase PFAS concentration and improve diffusion controlled electrolysis, to boost the naturally present salinity and to drastically reduce the reactor volume. Process systems engineering tools will be applied to define a hybrid integrated process. Thus, the proposed optimization model and techno-economic analysis are aimed at assessing the feasibility of PFHxA nanofiltration or reverse osmosis, coupled to electrolysis of the concentrate. Based on previous experimental data [1,3], we developed a pilot plant scale semi-empirical mathematical model describing PFHxA concentration by means of a cascade of *n* membrane stages and the BDD electrolysis of the concentrate stream. The hybrid process was optimized by determining the minimum total specific cost (TSC, $\$ \text{ m}^{-3}$), accounting the capital costs (CAPEX) and the operating costs (OPEX). The formulated nonlinear programming (NLP) was implemented in the General Algebraic Modelling System (GAMS).

The results obtained showed a drastic reduction in the TSC (76%) by means of the optimal 2-membrane stages-electroxidation integrated strategy and through the optimization of the process variables (Fig. 1). The reduction of the TSC was given by: (i) the cutback on CAPEX mostly due to the lower optimum electrode area and (ii), the reduction on OPEX mainly via the decrement of the required electrolysis time, which heavily affects the ELOX energy consumption, and the electrode replacement costs. Additional membrane stages increased the membrane system equipment capital costs, the pumping energy costs and the membrane replacement expenses, negatively affecting the TSC. These results demonstrate the benefits of membrane/ELOX process integration in the treatment of persistent organic pollutants, usually present in the low concentration range in impacted surface waters and groundwaters.

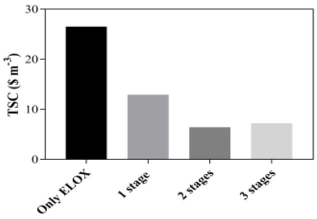

Figure 1. Comparison of the total specific cost of 1 – 3 membrane stages coupled to ELOX approach and the application of ELOX without pre-concentration for *2-log* PFHxA abatement.

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Is it worth using the electrodialysis/electro-oxidation system for the removal of pesticides? Process modelling and role of the pollutant

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As the global demand for food is rising so does the use of pesticides which in turn leads to a higher volume of wastewaters. Clopyralid is an organochlorine herbicide intensively used due to its wide range of applications. It is persistent in soil and its high solubility makes it very dangerous because it can reach the surface water by rainfall, spilling, leaching or the groundwater by infiltration. Although it can be degraded by microorganisms, clopyralid does not bound with suspended particles found in water and in absence of a substrate the biodegradation becomes difficult.

The development of new technologies, the use of new materials and different energy sources has been intensively studied in the last decades. Now, the attention is focused on the improvement of the existing technologies by combining them in order to achieve higher performances.

Concentration strategies gained a special attention lately because they offer the possibility of recovering materials or manage them as waste. Taking into account that clopyralid has ionic character a good way to concentrate it could be the use of electrodialysis. The use of ion exchange membranes offers the possibility to separate not only the ionic pollutant but also the excess of salts leaving the wastewater with less conductivity. The dilute stream can be discharged or either used in other process. The concentrated stream can be further treated, managed as waste or even submitted to a recovery process.

A good way to reduce the treatment cost and increase the efficiency is to integrate the electrodialysis with electro-oxidation (EO) and so to perform two processes in one-step. It was previously demonstrated by our research group that by combining these processes the transfer limitation is considerable reduced and the removal rate significantly increases when treating solutions containing 2,4-dichlorophenoxyacetic acid (2,4-D) [1].

The present work aims to demonstrate that the integrated electrodialysis-electrooxidation (EDEO) process not only increases the efficiency in the removal of the organochlorine pesticides from wastewater but also the minimization of the energy consumption. The system performance has been tested with clopyralid and the results compared with those obtained for 2,4-D. Moreover, the process has been modelled in order to explore the field of potential applications of the EDEO technology for the removal of polar organochlorine pesticides.

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Acknowledgments

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Application of WO_3 nanostructures synthesized by anodization in the photoelectrochemical degradation of pesticides

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In this study, WO_3 nanostructures have been synthesized using electrochemical anodization. Certain experimental conditions, such as the annealing temperature and atmosphere, have been varied in order to optimize the fabrication procedure and the photoelectrochemical properties of these nanostructures.

Annealing temperatures were modified between 400°C and 800°C, and the annealing process was carried out in different atmospheres, i.e., oxygen and argon. By analyzing the current density data obtained during the formation of these WO_3 nanostructures and, subsequently, by characterizing them using different techniques, it has been possible to optimize their synthesis. The composition and crystalline structure of the obtained nanostructures have been studied through Raman spectroscopy. Field Emission Scanning Electron Microscopy (FE-SEM) has been used to characterize their morphology, and electrochemical and photoelectrochemical tests have been performed to study the properties of WO_3 nanostructures.

Finally, these nanostructures have been used in the environmental sector, to degrade a recalcitrant and toxic pesticide called fenamiphos through the technique known as photoelectrocatalysis (PEC), using simulated visible light, in which electrolytic and photocatalytic processes are combined to mineralize the organic pollutant.

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Properties and Electrochemical Performance of Supported Pt(Cu) Core-Shell Catalysts for Hydrogen Oxidation

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Hydrogen oxidation reaction needs electrocatalysts to proceed at a suitable rate when hydrogen is used, for example, as a reactant in fuel cells. Nowadays, the catalyst of choice to promote this reaction is Pt, whose scarcity and high cost, alongside its low CO tolerance, justifies further efforts to develop alternative catalysts with lower Pt content and higher resistance to the CO. The strategy developed in our laboratory consists in synthesizing nanoparticles with a core-shell structure, where the cores are made from a sacrificial metal that is then covered by a Pt shell. In particular, carbon supported Pt(Cu) nanoparticles have been previously synthesized in our group by means of electrochemical deposition of Cu [1]. It has been shown that the Cu core exerts an electronic effect on the Pt shell, thus reducing the total amount of Pt required and, in turn, improving its CO tolerance. Nonetheless, powdery Pt(Cu)/C catalyst is needed to address the electrode manufacturing and, for this, chemical Cu^{2+} reduction methods are being developed. Different experimental procedures can be performed to synthesize supported Pt(Cu) nanoparticles in order to obtain an effective dispersion and the suitable particle size for their use as electrocatalysts in PEMFC and related technologies. It is also very important to choose the most adequate supports for the catalysts, as it has great influence on the catalyst performance, durability and efficiency.

In this work, carbon supported Pt(Cu) core-shell nanoparticles have been synthesized by electroless deposition of Cu, followed by a partial galvanic exchange with Pt. Different experimental procedures have been performed to obtain catalysts with a metal loading similar to that found in the commercial ones. Physicochemical characterization of materials, as well as their electrochemical characterization in a three-electrode cell, has been carried out. Cyclic voltammetry and the rotating disk electrode technique allowed the study of the oxidation of H_2 and H_2/CO mixtures.

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Sustainable electrochemical energy storage materials systems for off-grid, poor and remote communities

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The implementation of batteries to energy conversion systems in off-grid, poor and remote communities from all around the world, will overcome some of the technological challenges for electrification and large energy storage such as the difficult geographical accessibility and the modest scientific capabilities of isolated areas. The current ways of energy production to serve basic needs of these societies such as wood burning in non-ventilated spaces for cooking or the expensive kerosene for lighting are inefficient and insecure. So, the application of more effective, safer and environmentally friendly methods of electrical power is needed. Moreover, the use of clean and sustainable electrochemical energy storage systems such as batteries and supercapacitors coupled to solar and wind energy conversion technologies will also suppress the emission of green house gases produced by burning biomass or fossil fuels. Although the technological needs for electrification of both modern and remote communities are in principle quite different, the main challenge for the application of batteries to store the electricity produced by renewable sources is the same: *the development of advanced, scalable and inexpensive materials for safe, efficient, large-scale and sustainable electrochemical energy systems*. Consequently, to convert and store energy in isolated communities we must get profit from the knowledge and technologies produced during the last decades in the battery field and use it to overcome the current deficiencies. Herein it will show an overview of the latest efforts carried out by the scientific community on the development of sustainable and advanced electrode and electrolyte materials for clean electrochemical energy storage in batteries and supercapacitors.

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Study of the use of new ceramic materials for the removal of Norfloxacin by electro-oxidation in chloride media

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Norfloxacin (NOR) is an antibiotic widely used in veterinary and human medicine against gram-positive and gram-negative bacteria. The presence of antibiotics in the different water bodies represents a public health risk as they not only develop and increase the bacteria resistance to the antibiotic action, but also may cause specific damage to human health [1]. Additionally, the conventional process carried out in the wastewater treatment plants is unable to completely deplete antibiotics from the effluents. Consequently, new treatment processes are studied. Among them, electro-oxidation using boron doped diamond (BDD) anodes have shown good results. However, BDD anodes have a complex and expensive fabrication procedure that may complicate their use at high scale plants. On the contrary, ceramic electrodes with lower fabrication cost appear as an interesting alternative.

Previously, these ceramic electrodes have been successfully tested in sodium sulphate media showing good results [2]. The aim of this work is their study in a more common electrolyte, NaCl, where a lot of oxidant species coming from chloride oxidation are generated. Two ceramics electrodes based on $SnO_{2,}$ doped with Sb and Sb+Cu oxides, and a conventional BDD electrode, were tested as anodes for NOR degradation in an electrochemical reactor under different values of applied current densities (76, 114, 189 mA/cm^2).

From the evolution of the NOR decay profile with time using the different electrodes under study, it is shown that the first increase in the current density (from 76 to 114 $mA·cm^{-2}$) caused a growth in the degradation rate. However, this growth was not reflected when the highest current density was applied. This fact, together with the exponential trend showed in all the cases, is characteristic of a process under mass transfer control. It is worth to note that all the anodes employed achieved NOR degradation rates higher than 90%.

Regarding the total organic carbon (TOC) parameter, its evolution with time for all the applied current densities presented a slightly different trend as the higher the applied current density the higher the velocity of NOR mineralization in all the tested materials. This increase in TOC decay with the applied current in a process under mass transfer limitations is related to the higher amount of oxidizing species generated during the electrolysis. In this case, only the BDD electrode working at the highest applied current provided the complete mineralization, while the ceramic electrodes achieved a 80% (Sb-doped) and a 40% (Sb+Cu-doped) of mineralization for the same value of applied current. Therefore, the BDD presented the best behavior closely followed by the SnO_2-Sb doped ceramic electrode.

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Solar Photoelectro-Fenton Treatment of Mixtures of Tartrazine, Ponceau SS and Direct Blue 71 Azo Dyes

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Electrochemical advanced oxidation processes (EAOPs) are becoming a reality as new technologies for environmental remediation. These processes are based on the in situ generation of hydroxyl radicals ($^{\bullet}OH$), with a standard reduction potential of 2.80 V|SHE, thus being the second strongest oxidizing agent known after fluorine. The $^{\bullet}OH$ radical reacts with the organic pollutants, causing their overall mineralization or conversion into carbon dioxide, water and inorganic ions in most cases. Several studies have tested the performance of EAOPs for the mineralization of azo dyes. The existing literature is mainly devoted to the treatment of individual azo dye and few reports discuss the particularities of treating a mixture of dyes [1]. Therefore, the aim of the present work is to treat a mixture containing Tartrazine, Ponceau SS, and Direct Blue 71 dyes with 105 mg L^{-1} of total organic carbon (TOC) in 0.050 M Na_2SO_4 at pH 3.0 by electrooxidation with electrogenerated H_2O_2 (EO-H_2O_2), electro-Fenton (EF), and solar photoelectro-Fenton (SPEF). The experiments were carried out in a 2.5 L pre-pilot plant with a Pt/air-diffusion filter-press cell coupled to a solar planar photoreactor.

The degradation achieved by EO-H_2O_2 was not significant, which can be explained by the low oxidation ability of $^{\bullet}OH$ radical formed at the Pt anode surface. In this case, the Pt($^{\bullet}OH$) radical electrogenerated on the surface of the anode (Eq. 1) is partially transformed into the weaker oxidant PtO_x (Eq. 2), conferring it a lower oxidation ability. The color removal achieved by EF and SPEF with Fe^{2+} catalyst was quite similar because the main oxidant was the homogenous $^{\bullet}OH$ formed in the bulk from Fenton's reaction (Eq. 3). In all the treatments, absorbance decays during decolorization agreed with a pseudo-first-order reaction kinetics. In EF, the mineralization was only partial owing to the formation of molecules with high stability against hydroxyl radicals. In contrast, these by-products were rapidly photolyzed under sunlight irradiation in SPEF (Eqs. 4-5).

$$Pt + H_2O \rightarrow Pt(^{\bullet}OH) + H^+ + e^- \qquad (1)$$
$$Pt(^{\bullet}OH) \rightarrow PtO_x + H^+ + e^- \qquad (2)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (3)$$
$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (4)$$
$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \qquad (5)$$

In SPEF, eight short-chain linear carboxylic acids were detected, along with sulfate and ammonium ions from S and N atoms of the dyes, respectively. The effect of Fe^{2+} and azo dye concentrations, as well as the applied current density, was assessed. Total mineralization of azo dyes mixtures occurred when operating at concentrations up to 105 mg L^{-1} TOC with 0.50 mM Fe^{2+} at 100 mA cm^{-2}.

Acknowledgements

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Session 3. Wednesday 15 May 2019 (afternoon)

Schedule	Authors	Communication
14:30-14:45	*F. Santos, P. Almodóvar, C. Díaz-Guerra, J. Gonzalez, A. Molina, A. J. Fernández Romero*	Chromium (III) oxide-based materials as catalysts for ORR
14:45-15:00	*J. L. Nava*	Design of flow cells with parallel plates and rotating cylinder electrodes for electrometallurgical applications
15:00-15:15	*S. Santiago, S. Mena, I. Gallardo, G. Guirado*	Electrochemistry in ionic liquids: from CO_2 valorization processes to green smart devices
15:15-15:30	*E. Expósito, V. García, F. Gallud, A. Sáez, D. Valero, V. Montiel*	Electrocoagulation: A useful electrochemical technique regarding wastewater treatment
15:30-15:45	*L. A. Godínez, I. Robles, J. García, F. J. Rodríguez-Valadez, A. Ramírez, A. Rodríguez, D. Fernández*	Electro-Fenton based treatment of human waste; Towards the development of a drainage-free toilet
15:45-16:00	*J. J. Lado, E. García-Quismondo, J. Palma, M. A. Anderson*	Magnesium recovery from brackish water by capacitive deionization
16:00-16:15	*CA. Ponce de Leon, T. Schoetz, B. Craig, R.D. McKerracher, H.A. Figueredo-Rodriguez*	Green batteries
16:15-16:30	*D. C. Andrade, J. M. M. Henrique, V. J. P. Vilar, D. R. da Silva, C. A. Martínez-Huitle, E. V. dos Santos*	Novel reactive barrier concept coupled to electrokinetic remediation to remove hydrocarbon from soil
16:30-17:00	**COFFEE BREAK**	
17:00-17:15	*R. Salazar, L. C. Espinoza, D. Martins de Godoi*	Preparation of nanostructured dimensional stable anodes (DSA) for the electro-oxidation of oxamic acid
17:15-17:30	*P. Villegas-Guzman, F. Escalona-Durán, D. Ribeiro da Silva, C. A. Martínez-Huitle*	Electrochemical oxidation of antitubercular drugs in synthetic human urine
17:30-17:45	*A. Lejarazu-Larrañaga, S. Molina, J. M. Ortiz, R. Navarro, E. García-Calvo*	Circular economy in membrane technology: using end-of-life reverse osmosis modules for preparation of ion exchange membranes systems
17:45-18:00	*A.J. Motheo, R. Nakamura, M.F. Gromboni*	Electrochemical processes applied to treatment of aqueous medium containing a commercial preservative blend based on parabens
18:00-18:15	*E. Herrero, V. Briega-Martos, J. M. Orts, A. Rodes, J. M. Feliu*	Oxygen reduction reaction on acetonitrile containing solutions
18:15-18:30	*V. B. Lima, L. A. Goulart, M. R. V. Lanza*	Degradation of Ciprofloxacin in electrochemical cell using gas diffusion electrode (GDE)

Chromium (III) oxide-based materials as catalysts for ORR

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The most efficient materials to be used as catalysts for the oxygen reduction reaction (ORR) are noble metals, such as Pt or Pd. However, its high cost and low availability make necessary the study of new cheaper catalysts for ORR. In this sense, different transition metals have been tested to replace noble metals as catalysts in the ORR.

We have analyzed chromium (III) oxide supported on different carbonaceous substrates as catalyst materials for ORR. In this communication, a spectroscopic and electrochemical characterization of these electrodes will be shown together with the zinc-air batteries discharges using Cr_2O_3-based materials as positive electrodes.

Besides, we will show the Rotating Disck Voltammetric resulted for Cr_2O_3 nanoparticles as well as chromium (III) oxide supported onto graphite, graphene, and graphene oxide (GO). Interchanging electron values, n, ranging from 2 to 4 were obtained, indicating different ORR mechanisms depending on the Cr_2O_3-based material used. Finally, the experimental data will be modeled using an electrochemical-catalytic mechanism. A good agreement between modeled and experimental results has been obtained. Both theoretical and experimental results will be discussed in depth.

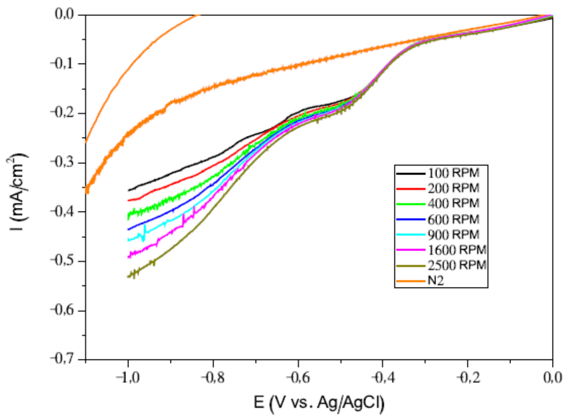

Figure 1. a) ORR study of Cr_2O_3 + GO.

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Design of flow cells with parallel plates and rotating cylinder electrodes for electrometallurgical applications

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The characterization of the reaction environment in continuous electrochemical reactors is necessary to optimize the operational conditions of electrolysis, such as hydrodynamics, current density, residence time, conversion of the electro-active species, among others. In this context, the mathematical modeling followed by experimental trials permit to construct reactors that guarantee the efficiency and yield of the desired reaction. In this work, we are interested in: (*i*) the design of a filter-press flow cell to be used in the evaluation of a nickel deposit on a mild-steel cathode and, (*ii*) in the design of a rotating cylinder electrode in continuous operation mode for the electro-recovery of silver. The goal is to minimize the edge effects at the inlet and exit of the cells. A theoretical analysis of current distributions was carried out, which were compared with experimental data of metal deposition. Tertiary current distribution analysis was made coupling the Reynolds Averaged Navier-Stokes equations with the *k*-epsilon turbulence model and the Launder-Spalding-like equations using wall functions. Different operational conditions (flow rate, applied current density, etc.) were evaluated. The cell and its components were printed in 3D from the CFD simulations. Primary and secondary current distributions were also calculated. The solution of the transport equations was obtained by using a commercial software via finite element method.

Electrochemistry in Ionic Liquids: from CO_2 valorization processes to Green Smart Devices

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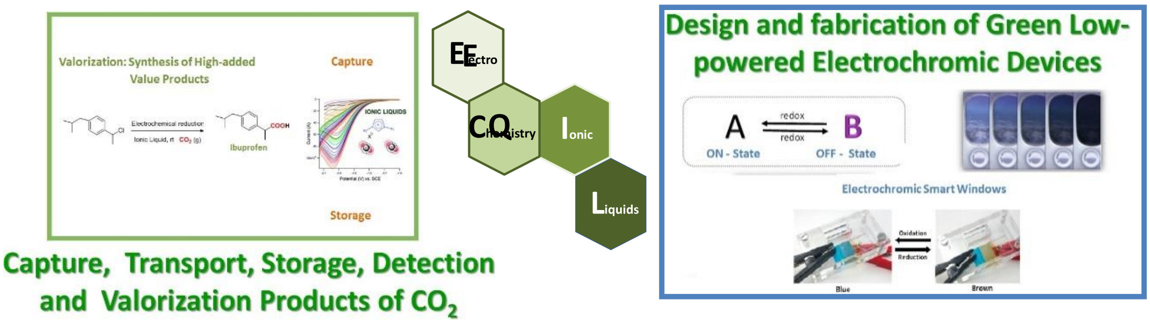
Ionic Liquids (ILs), which are solvents exclusively composed by ions, are one of the most popular family of Green Electrochemical Solvents, since they have negligible vapor pressure, wide temperature range at liquid phase, high electrochemical stability, and relatively high ionic conductivity[1]. These amazing features allow to ILs have a lot of applications, from its use as enabling solvents for chemical processing, including reaction media for acid scavenging, addition reactions, and catalytic transformations, to its use as solvents (substituting the supporting electrolyte) in electrochemical synthesis and characterizations and its use such as electrolyte in batteries and devices[2–7].

In this communication, we describe two different applications that we perform in our research group with the synergistic use of electrochemical techniques ("Green Technologies") and ILs ("Green Solvents"). The first one aims to design an environmentally friendly route to obtain Ibuprofen ((RS)-2-(4-(2- methylpropyl) phenyl) propanoic acid) through an electrocarboxylation route using CO_2 and ionic liquids. The second approach demonstrates the use of ionic liquids in the fabrication of smart devices based on photoelectrochromic compounds, such as spiropyrans. The "green" synthesis of those derivatives and fabrication of devices would open a suitable environmentally friendly process for design electrochemical synthesis of pharmaceutical products and smart devices.



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Electrocoagulation: A useful electrochemical technique regarding wastewater treatment

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Electrocoagulation is an electrochemical technology similar to conventional chemical coagulation. However, the main feature of the electrocoagulation is that the coagulant agent is generated through the application of an electric current to an anode, so-called “sacrificial anode”, usually made of aluminium or iron. During the electrocoagulation process, the coagulant substance is generated in situ. Thus, the following stages can be considered:

1. Formation of the coagulant agent due to electrochemical oxidation of the sacrificial electrodes.
2. Destabilization and of contaminants, particles in suspension and emulsions breaking down.
3. Formation of macro-aggregates of destabilized substances leading to floccule formation.

In addition, electrocoagulation is a compact, versatile, efficient, selective, safe, robust and easily automatable technology, which can replace sophisticated treatment processes that require large volumes or a large amount of chemical reagents as is the case of traditional wastewater treatment plants. As a result, the cost of effluent treatment decreases substantially. In conclusion, electrocoagulation technology is inexpensive and effective for wastewater treatment prior to its discharge or reuse.

The “Applied Electrochemistry and Electrocatalysis” Group of the University of Alicante has worked on the improvement of this technology´s application regarding the treatment of wastewater coming from different industrial sectors. For this purpose, the focus in the work has been set on:

- The design of an electrocoagulation tank that improves operational aspects as: foam separation, sludge separation, the homogeneous corrosion of the sacrificial anodes and the minimization of corrosion of the electrical contacts.
- Direct electric power supply of the electrocoagulation reactor using photovoltaic modules that allows the use of electrocoagulation systems in remote places without connection to conventional electric grid.

The research done by the research group in the last years using wastewater from a large number of companies from different sectors such as: residue leaching, agro alimentary sector, almond scalding, milk sector, plastic recycling, vehicle washing, galvanizing sector, biodiesel, slaughterhouses and urban sewage treatment plants, made possible to test this technology.

These experiences allowed the research group to establish with a high degree of certainty the success rate of the electrocoagulation technology application regarding wastewater treatment coming from different industrial sectors.

Electro-Fenton Based Treatment of Human Waste; Towards the Development of a drainage-free Toilet

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Drainage, is with no doubt, one of the milestones in the evolution of human societies and in spite of its widespread use, approximately 2,600 million people in the world and close to 9 million in Mexico, currently live in places that not only lack this infrastructure, but also the resources to generate it.

In this context, and that of the investment that must be made to provide drainage to the population that still needs it, the development of a drainage-free toilet is an important and socially useful challenge.

In this talk, the results on the development of a drainage-free toilet will be presented. The competitive advantage of this technology lies in the use of an electro-Fenton based reactor[1] that, unlike other currently available approaches, is capable of eliminating parasites and pathogens to provide clean water that can be used for washing, rinsing or watering plants and gardens.

It is worth pointing out that this device works with electrochemically-generated strong oxidant species and that in this regard, is essentially different from a dry toilet or a septic tank. In these approaches that are currently widely employed, the mechanism is to contain and partially neutralize the infectious materials, and eventually, it is always necessary to collect and transport the waste to an appropriate treatment facility.

The toilet that will be discussed is patented and works with relatively low costs since it does not contain expensive elements or materials and does not use electricity since it works with solar energy.

The approach to a toilet that completely eliminates contaminants in the same site of its installation, will be part of an environmentally friendly market with a potential of approximately 8,000 million dollars a year[2]; worldwide. This estimate is derived from projections that consider its use in rural households, low-income urban housing, mobile and portable facilities for camps and disaster areas, and a market in high-income buildings and houses that are designed with environmental concepts in mind.

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Magnesium Recovery from Brackish Water by Capacitive Deionization

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Capacitive Deionization (CDI) is a promising electrochemical water treatment technology that has drawn a lot of attention in the last decade. CDI mechanism is based on the adsorption of charged particles (ions) in the electrical double layer of porous carbon electrodes. Using the charge/discharge dynamic of a supercapacitor, CDI is able to deliver water with a certain quality while storing part of the energy supplied in the charging/ion adsorption process. CDI has been mainly studied as a brackish water desalination technology in the last ten years. Nevertheless, ion separation applications such as nitrate removal[1], heavy metal recovery[2], lithium extraction[3] or vanadium[4] separation has been also proposed as new features.

At the same time, the extraction of minerals and metals from water resources (including desalination brines) using cost-effective and high efficient and effective recovery processes has emerged as a new relevant topic. Among the main components of water sources and brines, magnesium has been included in 2017 in the list of critical raw materials (CRMs) elaborated by the European Commission. That means that magnesium has been identified as a crucial raw material for the European economy. With the aim of addressing the access to this component, a methodology based on CDI has been proposed in this work. The idea consisted on employing a semi-industrial CDI pilot plant using brackish water as feeding solution as an electrochemical treatment for separating and concentrating magnesium.

Experiments were performed in a 5-cell CDI pilot plant using multicomponent electrolytes (Case A. Na^+ and Mg^{2+}; Case B. Na^+ and Ca^{2+}; Case C. Na^+, Ca^{2+} and Mg^{2+}) in a single pass configuration in order to evaluate the potential of CDI as a separation technology. Results indicated that CDI has the potential to separate magnesium from brackish waters in different effluent fractions. More specifically, Ca^{2+} could be concentrated 40 % (vs Na^+) and Mg^{2+} up to 70 % (vs Na^+) in the case of dual cation component (Case A and B) electrolytes. Similar adsorption/desorption kinetic trends were observed for Ca^{2+} and Mg^{2+}. Moreover, when a multicomponent electrolyte was treated (Na^+, Ca^{2+} and Mg^{2+}), singular fractions were identified in which Ca^{2+} and Mg^{2+} could be separate/concentrate. Ion adsorption/desorption mechanism along the CDI experiment such as physical adsorption, electrochemical adsorption and faradaic reactions were identified and studied.

Based on the information extracted from the CDI experiments a suitable treatment sequence for concentrating different ions was proposed. The idea behind this methodology would be the reassessment and valorization of different water sources.

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Green batteries

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Current mobile electronic equipment require batteries that are able to provide high-performance and large energy storage. Although this demand is reasonable satisfied with lithium – ion batteries, longer battery times are required. In addition, the demand for rechargeable batteries for vehicle applications is still not affordable for the majority of the population. Moreover, nowadays society demands are not limited to high performance but also demands low costs and recyclability with minimum or not damage to the environment. The future of our society might depend on finding inexpensive environmentally friendly battery materials that are able to provide high energy and power densities. Since there is always a large difference between the theoretical and practical capacities in most batteries, there is large amount of waste material that remains unused. Modern "green" batteries require the use of nanostructured materials to avoid waste and to increase performance. This talk provides an insight into the requirements of a "green battery" and provide some possible examples including the aluminum – polymer and the iron - air batteries.

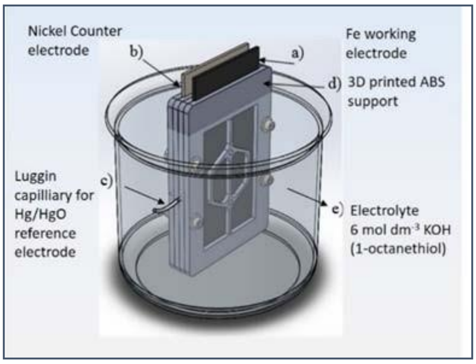

Figure 1. Experimental cell arrangement of an iron-air battery.

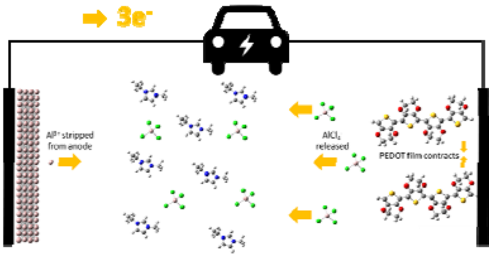

Figure 2. Aluminium-polymer battery

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Novel reactive barrier concept coupled to electrokinetic remediation to remove hydrocarbon from soil

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In this work, a novel, original and ecological alternative to treat soils contaminated with diesel was proposed. Coupling two well-known technologies, electrokinetic remediation and permeable reactive barriers (PRBs), the depollution efficiency was evaluated; however, the originality of PRBs concept is the use, for first time, of cork as the main barrier were composition. The barrier was placed into the soil in different sections anode, central and cathodic compartments to favor the retention and adsorption of hydrocarbon due to the migration/diffusion effects promoted from soil to the anode during the electrokinetic remediation (ER). For this reason, SDS was used as supporting electrolytes in cathodic reservoirs, in order to promote the mobility of organic compounds through the soil and consequently, decreasing the treatment time and costs. Additionally, the influence of direct current (DC) and reverse polarity (RP) approaches for applying electrical fields were evaluated for removing hydrocarbon from the soil. Results clearly indicated that, the novel PRBs concept was efficient when coupled with ER because higher hydrocarbons removals were achieved. During ER coupled to cork barriers, it was observed that the use of SDS and RP contributed positively to the transport of total petroleum hydrocarbons. At the end of the 20 days of depollution treatment, the cork contributed to increase the removal efficiency of hydrocarbon due to adsorption phenomena. Therefore, this technology provided a global treatment to soil without following treatments of the contaminated effluents.

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Preparation of Nanostructured Dimensional Stable Anodes (DSA) for the electro-oxidation of oxamic acid

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The dimensionally stable anodes (DSA) have been widely used by the chlor-alkali industry since active chlorine species are generated in these surfaces whose generation will depend on the pH of the medium[1]. These electrodes consist of a titanium support on which is deposited an oxide or a mixture of oxides of Ir, Ti, Ru, Sn, Pd which is electrically conductive[2]. Different methods of synthesis have been developed such as Pechini, spin-coating and thermal decomposition, among others.

In the present work, the synthesis of nanoparticles (NPs) of IrO_2, RuO_2 was performed to obtain DSA electrodes, which were used to degraded oxamic acid. Two types of DSA named Class I and II were prepared, both of which were obtained from the modification of a Ti sheet from the painted with commercial TiO_2 NPs and IrO_2 and RuO_2 NPs of own synthesis. For the class I DSA the NPs used were synthesized separately, while for the class II electrode Nps were synthesized in the same reaction medium. Electrolysis were carried out in an open cylindrical cell without division at 25°C. Every DSA was used as anode and a stainless steel as cathode, both with a geometric area of 2.8 cm^2 immersed in 0.05 M Na_2SO_4 or NaCl and applying a current density of 3 mA cm^{-2} for six hours. Decay of compound concentration was followed by ion exclusion chromatography and mineralization by decay of total organic carbon (TOC). Fig. 1a shows that in Na_2SO_4 there was no degradation of the compound, however, in NaCl it is possible to decrease the oxamic acid concentration and it is higher with class I DSA. With both electrodes, degradation follows a pseudo first kinetic (Fig. 1b) where the class I electrode in NaCl presented an apparent kinetic constant five times higher than that obtained with the class II DSA (2.58×10^{-5} *vs* 5.08×10^{-6} s^{-1}) under the same experimental conditions. The same tendency is obtained in the TOC variation showed in Fig. 1c where class I DSA allows reaching a higher mineralization close to 70%. A greater degradation and mineralization is achieved with the class I electrode in NaCl because by ion chromatography it was detected that with this DSA, hypochlorite ion is generated in a higher concentration than with class II DSA, while with the second electrode, chlorate ion, which is an oxidant less strong than the hypochlorite ion, is generated in a higher concentration.

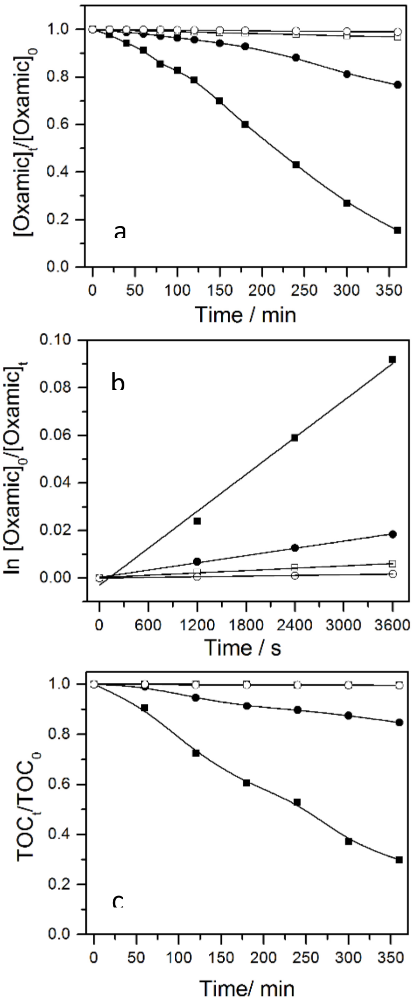

Figure 1. (a) Oxamic acid degradation, (b) kinetic of pseudo first treatment (c) TOC variation. Class I DSA NaCl: ■ , class II DSA NaCl:•, class II DSA Na_2SO_4: ☐,class II DSA Na SO : ○

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Electrochemical oxidation of antitubercular drugs in synthetic human urine

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Antibiotics are a major concern around the world. They are being accumulated in the environment for different reasons, from which excretes can be highlighted. For instance, for each supplied dose of Isoniazid (INH) and Rifampicin (RIF), first-line anti-tuberculosis antibiotics, 50-70% and up to 30% of them, respectively, are excreted within the next 24 h in the urine. Thus, considering that on average, a single person discharges 1.5 L of urine per day [1], an under-treatment person represents an important source of antibiotics that are released into the environment. Therefore, the development of environmentally friendly, cost-effective and easy-to-operate technologies to approach an efficient treatment of complex matrices such as urine is a main challenge in the area of environmental sanitation. In this context, this work aims to address the application of technology in the degradation of antibiotics.

The electrochemical degradation of the antibiotics RIF and INH in synthetic human urine (SHU), using boron diamond doped (BDD) and Ti/Pt anodes, was evaluated. A complete electrochemical elimination of both antibiotics at 15 mA cm^{-2} was achieved, evidencing the catalytic properties of each one of the anodes. The oxidation pathways, which are highly dependent on the electrode material [2], were also investigated: 1) the electron transfer from RIF and INH to the upper oxide formed at the Ti/Pt anode, 2) the indirect oxidation of RIF and INH by the electro-generated hydroxyl radicals at the BDD anode, and 3) the indirect reaction between RIF and INH and secondary oxidant species electrochemically formed from the ions of the matrix, mainly from chloride that is highly concentrated at the SHU [3]. Meanwhile, the pH conditions play a fundamental role in the predominance of both oxidant species electrogenerated and the chemical structure of the antibiotics, and then, the electrochemical treatment of the SHU contaminated with RIF/INH was performed at three different initial pH conditions (3.0, 4.0 and 6.5). To establish the extension of the treatment, the by-products evolution was investigated as well as biological tests that evidenced the electrochemical oxidation as a promising technique to eliminate the mixture of RIF and INH in the SHU.

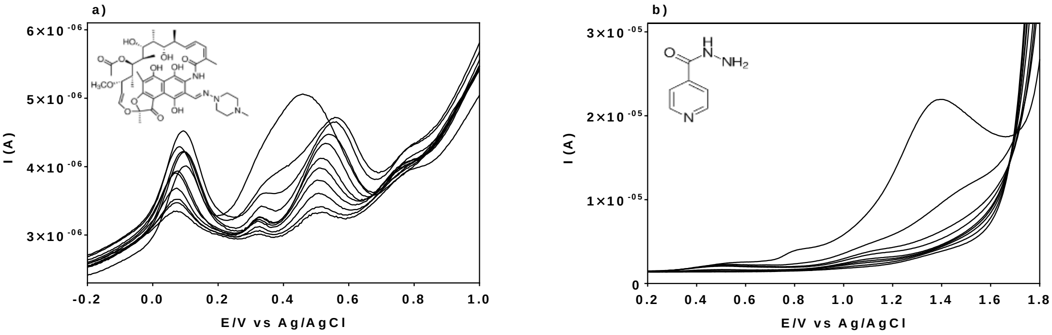

Figure 1. a) RIF and **b)** INH evolution determined by differential pulse voltammetry (DPV) by using GC and BDD electrodes, respectively, during the electrooxidation of the mixture of antibiotics by applying 15 mA cm^{-2} with BDD anode.

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Circular economy in membrane technology: using end-of-life reverse osmosis modules for preparation of ion exchange membranes systems.

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Membrane technology is a highly developed separation and purification technology. Among other membrane processes, reverse osmosis (RO) is the most widely used. However, fouling causes a shorten membrane lifespan, thus it is estimated that >840,000 RO modules are discarded in landfills every year [1]. To boost the sustainability in membrane technology, the recycling of end-of-life RO modules has been investigated in the last years [2]. In this study an innovative recycling alternative as ion exchange membranes and polypropylene components for the electrodialysis (ED) stack is proposed. Ion exchange membranes are prepared by casting and phase inversion method using recycled membranes as mechanical support. Polypropylene parts of the RO module are recycled to construct most of the components of the ED stack (i.e. compartments, end plates, separators).

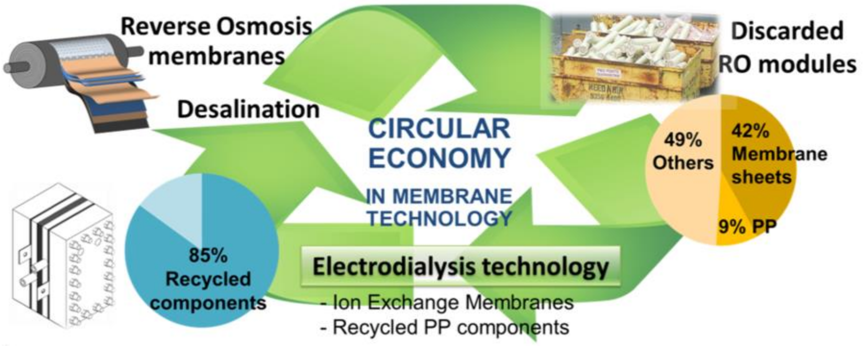

Figure 1. Diagram of the proposed strategy for end-of-life RO modules recycling into electro membrane systems.

The electrochemical properties of the membranes are analysed in order to select the optimum membrane preparation conditions. By this technique, membranes with a high permselectivity (87%, similar to commercial membranes) and enhanced mechanical stability have been obtained. The electrical resistance is higher than commercial ones ($77.26\ \Omega\cdot cm^2$), so further research should be carried out in order to decrease this parameter. The technical viability of the recycled membranes has been tested by desalination experiments in a four unit cell electrodialysis, which has been constructed using recycled plastic (i.e. around 90% weight of the ED stacks is made of recycled polymers). The desalination process achieved 84.5% of salt removal by circulating 12,808 $kCul\cdot m^{-3}$, this entails a production of 4.67 $L\cdot m^{-1}h^{-1}$. In this work, an attempt to conduct membrane technology towards a circular economy has been disclosed, and this approach is aligned with applications such as heavy metal recovery from mining waters, treatment of leachate mixtures from landfills, nutrient recovery from waste waters, valorisation of brines or waste water treatment using microbial electrochemical technology.

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Electrochemical processes applied to treatment of aqueous medium containing a commercial preservative blend based on parabens

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Concern about the degree of contamination of different water sources has led to a growing number of studies on the degradation of different contaminants in aqueous media. The degradation of preservatives used by the cosmetic industry has been much studied[1], mainly due to the characteristics of the endocrine disruption attributed to the parabens[2]. Currently, the cosmetics industries have a wide range of formulations for the conservation of the various products produced. However, the cost of preservatives is one aspect that has kept formulations containing parabens in use. Among these formulations, Phenonip ™ P4 from Clariant is a preservative blend with a broad spectrum of antimicrobial activity. Thus, this work focuses the electrochemical degradation of Phenonip ™ P4 with chemical composition of phenoxyethanol (70 – 75 % w/w) and parabens (methyl 14.5 – 16.5 % w/w, ethyl 3.7 – 4.3 % w/w, propyl 1.7 – 2.3 % w/w and n-butyl 5.7 – 6.3%).

The electrolyzes were carried out using commercial mixed metal oxide (MMO) anodes (DSA$^{®}$ from De Nora, nominal composition Ti/Ti$_{0.7}$Ru$_{0.3}$O$_2$) in a filter press electrolysis cell with a quartz window. With this cell, it is possible to operate in the dark (electrochemical mode) or irradiated by an UV-visible lamp (photo-assisted mode). In addition, the degradation was performed using flow reactor model ECWP d20X5P (Condias GmbH) with boron doped diamond (BDD) anodes. Using the MMO anodes and NaCl as supporting electrolyte, at concentrations of 0.1, 0.05 and 0.01 mol L^{-1}, the removal of parabens (e-PHBA) during 120 minutes electrolysis (electrochemical mode at 100 mA cm^{-2}) was 96, 75 and 30%, respectively. On the other hand, the removals of phenoxyethanol (PhE) in the mixture under the respective conditions were 96, 85 and 50%. Considering that the concentration of 0.1 mol L^{-1} NaCl promotes the greatest removal of all components of the blend, it was used in exhaustive electrolysis at current densities of 50, 75 and 100 mA cm^{-2}. The electrolysis times required for the removal of the different components of the blend decrease with increasing current density. In addition, when the photo-assisted mode is used the removal is more efficient. The observed behavior in the removal of e-PHBA and PhE was the same for all the electrolysis, with the PhE being removed before the e-PHBA. Using BBD electrodes and Na$_2$SO$_4$ as the supporting electrolyte, at ionic strength of 0.1, 0.01 and 0.001 mol L^{-1}, the removal of e-PHBA during electrolysis of 180 minutes (electrochemical mode at 30 mA/cm^2) were respectively 99, 97 and 96 %. On the other hand, the PhE was totally removed in the blend under these conditions. Considering that the ionic strength of 0.1 mol /L caused the greatest removal of all components of the blend, it was used in exhaustive electrolysis at current densities of 20, 30 and 45 mA cm^2. The complete mineralization of blend components was achieved with a charge of 14.7 A h dm^{-3} for all current densities used.

Using commercial MOM anodes, with and without irradiation, the performance for the removal of the contaminants depends on the supporting electrolyte concentration. However, with BDD anodes, the mineralization is achieved and the dependence with the electrolyte concentration is low.

References

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Oxygen reduction reaction on acetonitrile containing solutions

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Oxygen reduction reaction has been widely studied because it is a key reaction in devices for energy conversion such as fuel cells and lithium-air batteries. Most of the studies have been carried out in aqueous solutions but in Li-air batteries, aprotic solvents should be used. Therefore, understanding the effect of the use of an organic solvent on the reaction is now a requirement for the deployment of energy efficient devices. Moreover, a deep knowledge of how organic solvent molecules interact with the surface and how the presence of these molecules affects the reaction mechanism is required to optimize the performance of these devises. Among all the possible organic solvents, acetonitrile is probably the simplest organic molecule that can be used for this purpose.

In order to understand the effect of the presence of acetonitrile, it is important to characterize the adsorption mode. For this purpose, the adsorption of acetonitrile has been studied on platinum single crystal electrodes in acidic and alkaline solutions. Cyclic voltammetry results show that adsorption processes are structure and pH sensitive. The combination of in situ infrared measurements and density functional theory calculations allow to propose possible adsorbed species for the different potential values. The results obtained from these studies has been used to analyze the reactivity of platinum in these media for the oxygen reduction reaction, obtained using the hanging meniscus rotating disk electrode configuration. The major effects are the diminution of the limiting current densities and the shift of the onset potential to lower values as the acetonitrile concentration increases. These results will be interpreted considering the proposed adsorption modes of acetonitrile.

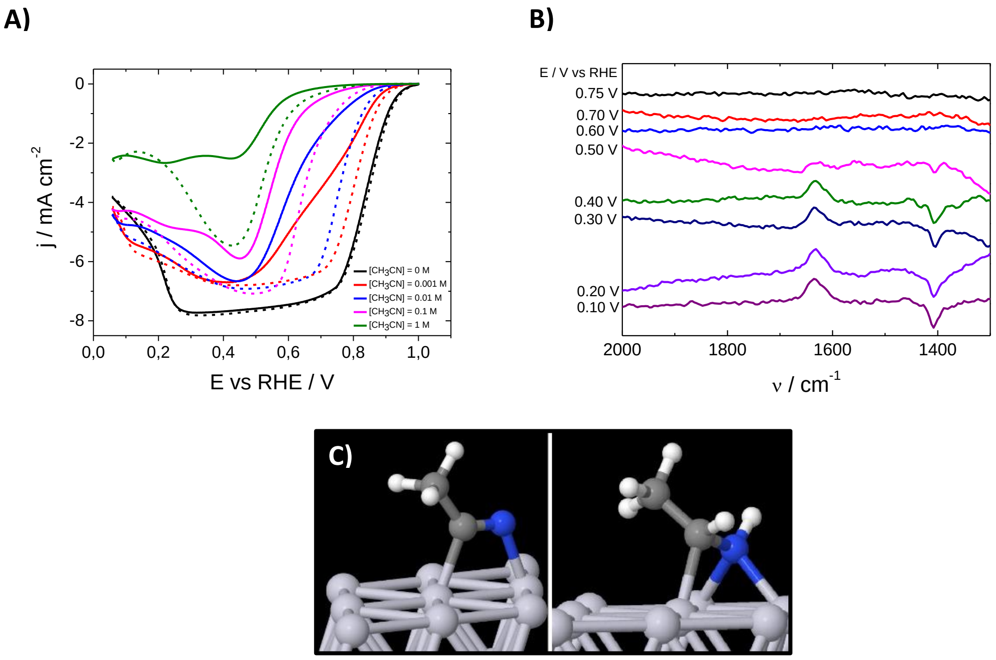

Figure 1. A) Cyclic voltammetry of the ORR at Pt(111) in 0.1 M $HClO_4$ + 1 mM CH_3CN using HMRDE; $\upsilon = 50$ mV s^{-1}, $\omega = 2500$ rpm. B) In situ infrared experiment using Pt(111) in 0.1 M $HClO_4$ + 1 mM CH_3CN with p-light; $E_{ref} = 0.75$ V. C) Adsorbed acetonitrile (left) and reduction product ethanimine (right) structures at Pt(111) from DFT calculations.

Degradation of Ciprofloxacin in electrochemical cell using gas diffusion electrode (GDE)

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The emergent pollutants are extremely resistant to traditional effluent treatment processes, but can be removed by the use of advanced oxidative processes (AOP), which are based on the generation of highly reactive species (hydroxyl radicals), from hydrogen peroxide (H_2O_2), which degrade persistent pollutants. H_2O_2 can be electrogenerated in situ by the oxygen reduction reaction (ORR) in the reaction medium. The use of highly porous gas diffusion electrodes (GDE) promotes the supply of oxygen at the electrode / solution interface and can increase the speed of the ORR [1,2]. The present work aimed to study the degradation of the drug Ciprofloxacin by different AOP systems using a electrochemical cell with GDE. The degradation assays were performed in an electrochemical cell, investigating the direct (N_2) and indirect electrochemical processes in the H_2O_2, H_2O_2/UV, Electro-Fenton and Photo-Electro-Fenton systems. The degradation of the concentration of the studied drug was evaluated in a high efficiency chromatograph (HPLC) and the mineralization efficiency was evaluated by the total organic carbon (TOC) analysis. Among the systems studied, the best degradation efficiency of Ciprofloxacin was Photo- Electro-Fenton, resulting in a higher percentage of mineralization of 54.8%, 100% degradation rate and a lower energy consumption of 4,110 kWh kg^{-1} TOC. The degradation of the less efficient compound was recorded in the application of UV light to the system, presenting a removal of only 1.0% of organic compound in the medium. The H_2O_2, H_2O_2/UV, Electro-Fenton and Photo-Electro-Fenton couplings showed 100% removal rate, varying the mineralization and energy consumption of the compound, which were 26.0% and 7,908 kWh kg^{-1} TOC (H_2O_2); 28.0% and 8,693 kWh kg^{-1} TOC (H_2O_2/UV) and 28% and 7,845 kWh kg^{-1} TOC (H_2O_2/Fe^{2+}), the results are presented in Figure 1. However, due to the high rate of oxidation of the drug and low energy consumption, in the Photo-Electro-Fenton process, the coupling of this system proved to be an excellent electrocatalyst for the generation of hydroxyl radicals in the medium, being promising for the treatment of wastewaters with organic pollutants.

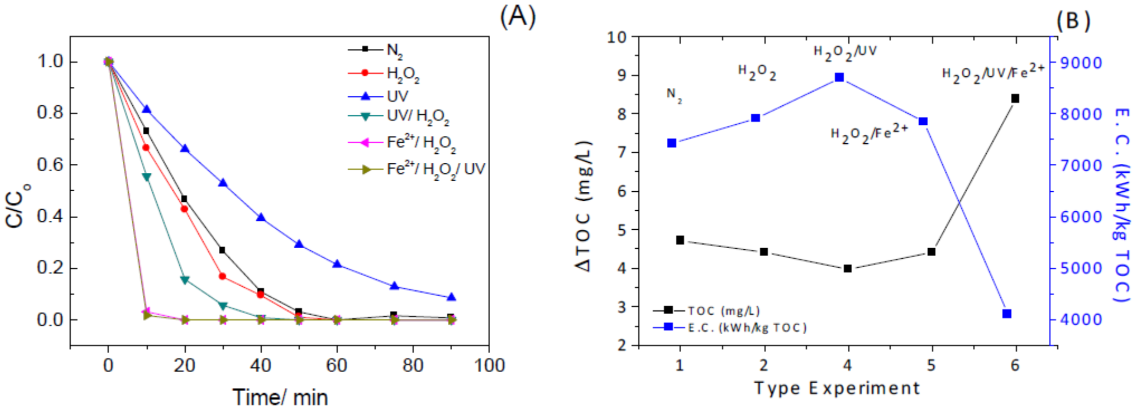

Figure 1 – (A) Ciprofloxacin degradation rate (30 mg L^{-1}) obtained in GDE oxidative processes at current density of 50 mA cm^{-2}, 0.1 mol L^{-1} K_2SO_4 electrolyte at pH 2.5, for 90 min. (B) Energy consumption (EC) and TOC variation in different degradation systems of Ciprofloxacin (30 mg L^{-1}) using GDE as working electrode, in electrolyte K_2SO_4 0.1 mol L^{-1}, pH 2.5 (H_2SO_4).

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