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**WCCE11 - 11th WORLD CONGRESS OF
CHEMICAL ENGINEERING**

IACCHE - XXX INTERAMERICAN CONGRESS OF CHEMICAL ENGINEERING
CAIQ2023 - XI ARGENTINIAN CONGRESS OF CHEMICAL ENGINEERING
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Erratum

Abstracts not included in the final version



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Techno-economic analysis and pyrolysis of the energycane *Saccharum spontaneum* for bio-oil production

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The present work aims to evaluate through a techno-economic analysis the viability of the pyrolysis process using an energycane variety, *Saccharum spontaneum*, for bio-oil production. The process was modeled by Aspen Plus V10 using a kinetic model scheme. 100 kg/h of this biomass mixed with water (10:1 w%) at 25 °C and 1 bar were considered as the mainstream which enters a continuous-stirred tank reactor (CSTR), with satisfactory approximation to reality [1], coupled with a pump system and a boiler. The thermodynamic packages chosen were: NRTL for the liquid and Peng-Robinson/Lee-Kesler for the gases. The Poynting factor was also considered to deal with the non-ideality under high pressure, taking p-xylene as the main component in bio-oil. The overall pyrolysis was modeled by a single-step model at 40 bar and 450 °C producing a gaseous phase formed by H₂, CO, CO₂ and H₂O, a liquid phase (bio-oil), and a solid phase (bio-char). The biomass substitution formula was given by the proximate/ultimate analysis [2] and the stoichiometric coefficients of all the components were obtained through their molar masses. The kinetic parameters considered were 163.7 kJ/mol for the activation energy and 10.8 s⁻¹ for the logarithm of pre-exponential factor as informed in the literature. In these conditions, the bio-oil production was 60.7 kg/h at 40 bar and 250 °C. Regarding the economic analysis of this plant, the set of equipment to estimate the fixed capital cost was comprised by a stainless steel reactor, two cast-iron simple-effect pumps, two carbon-steel boilers and a 13-inch wet cyclone, obtaining a CAPEX of US\$ 708,152.00 approximately. For a payback of two years, the future value of OPEX was US\$ 1,694,715.00 and the break-even point for the bio-oil was US\$ 2.64 per liter. Fixing its price at US\$ 2.90/liter, in ten years of plant operation, the internal rate of return was 29%, obtaining an EBITDA of nearly US\$ 2,187,017.00 with a net profit of US\$ 1,891,743.00. The results showed that this investment was favorable, considering a minimum attractive rate of return of 15%, but the bio-oil sold was not competitive with its international price. Therefore, this work suggests the need to explore other routes such as catalytic pyrolysis, using zeolites such as ZSM-5, to improve the quality of the bio-oil produced or other energetic integration pathways to make it competitive compared with the bio-oil price reported elsewhere.

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The challenges of Upscaling FTO-assembled Photoelectrochemical Devices

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Objective: Third-generation photovoltaics, such as dye-sensitized solar cells (DSSC) and Perovskite solar cells (PSC), are becoming significant contenders for the solar market due to their ease of assembly, low-cost materials, and prospective for building application and integration [1]. The architecture of the devices comprises Transparent Conductive Oxide (TCO) substrates for the optical and electrical properties, which allow sunlight wavelength transmission and current extraction from the device. One disadvantage of scaling up DSSC and PSC is the lack of conductivity of the TCO, which prevents the photoelectrochemical conversion (*PCE*) from being maintained as the area of the solar cell increases. One solution is to improve the TCO's conductivity by adding current collectors to the substrate, such as metal grids [2]. However, the abrasiveness of solar cell components (electrolyte, perovskite) towards metal may jeopardize the collectors' long-term functionality. In this work, we propose fluorine-doped tin oxide (FTO) coated glass substrates with FTO current collectors since the material is mechanically and chemically compatible with the solar cells' architecture.

Materials and Methods: Simulations of charge collection were performed using COMSOL Multiphysics. Substrates were produced by masking FTO coated glass with heat resistant paint and laser patterning the design. Afterwards, the FTO-collector was deposited by ultrasonic spray pyrolysis. Finally, the mask is dissolved by KOH solution.

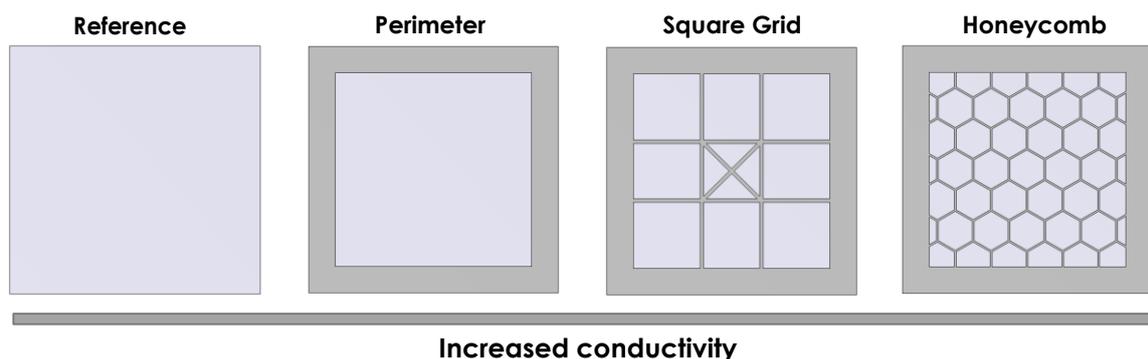


Fig.1. FTO-collector designs simulated for charge extraction.

Results and Conclusion: By experimenting with different geometry and size, we obtained a honeycomb FTO-collector substrate that increased the *PCE* of 25 cm² DSSC by three times. The findings demonstrate the feasibility of FTO-collector substrates for upscaling solar cells and the adaptability to any technology built on FTO-coated substrates.

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Cycling ageing analysis in 18650 batteries at low temperature

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Decarbonization efforts are motivated due to the need to reduce greenhouse gas (GHG) emissions and to anticipate the depletion of fossil fuels. Transport sector is one of the largest GHG producers where it is most difficult to reduce GHG emissions. Lithium-ion batteries currently represent an excellent alternative to meet the growing demand for energy storage and the electrification of the transport sector. However, there is still a considerable amount of research on degradation mechanisms to be performed to predict remaining lifespan. Ageing mechanism of Li-ion batteries are a complex multi-causal process strongly affected by temperature. Ageing mechanisms could be grouped into three degradation modes: Loss of Conductivity (LC), Loss of Active Material (LAM) and Loss of Lithium Inventory (LLI). In this work, we studied the cycling ageing of 18650 commercial NMC lithium-ion batteries at 10°C. For this purpose, we carried out life cycle tests at different charge and discharge c-rates (Fig.1). We also performed galvanostatic Intermittent Titration Technique (GITT) (Fig. 2) tests in the voltage range for charge and discharge process for different state of health (SoH). In order to perform GITT experiments, a short current pulse of current 1 A for charge and 3A for discharge was applied for a transient time of 13 min and 4 min, respectively; followed by a relaxation time of 30 min, which is required for achieving electrochemical equilibrium for the system. Tests were performed on the Gamry Interface 5000E™ potentiostat/galvanostat. Furthermore, we performed Electrochemical Voltage Spectroscopy studies through incremental capacity (IC) curves. IC curves peaks are associated with batteries phase transformations due to ageing phenomena and each peak has a unique peak height, area, and position associated with a degradation mode. This research focuses on IC curves derived from discharge capacities. Deconvolution was carried out from these curves from Gaussian adjustments, determining the area, position, and height of resulted peaks. The height of the IC peaks decreases over cycle number, and it is observed a shift of IC peak position towards lower voltages. Peak at the lowest potential position results as an interesting health indicator for degradation evolution. Thermodynamics and faradaic effects were identified (Fig. 3). As a conclusion, LLI was identified as a critical degradation mode in the first cycles while LAM effects were depicted during last cycles.

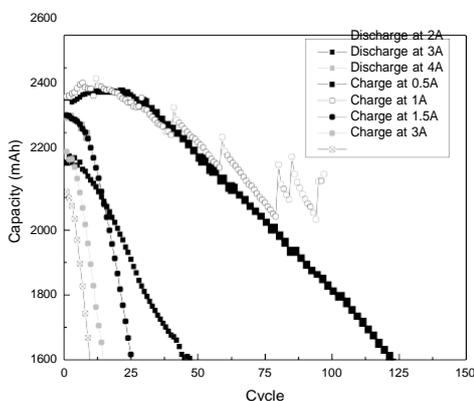


Fig. 1.- Life cycle tests at different charge and discharge c-rates

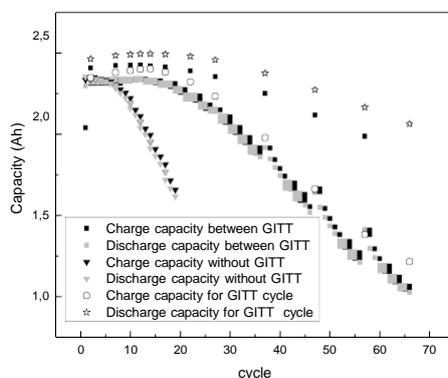


Fig. 2.- Charge and discharge capacity before and after GITT at 1A and 3A charge and discharge current, respectively

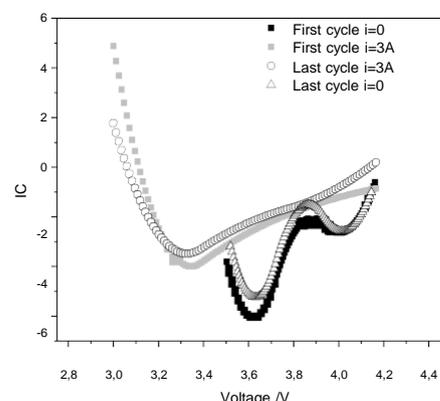


Fig. 3.- Incremental capacity (IC) curves

Ethane recovery in gas processing plants: Conceptual design of the adsorption separation cycle

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Ethane is the main feedstock for ethylene plants. It represents a large fraction of the hydrocarbons found in the natural gas liquid (NGL) extracted in natural gas (NG) processing. The conventional ethane extraction technology (GSP) is based on cryogenic distillation which is an energy intensive process. An alternative separation through an adsorption process is challenging. Ethane (C₂) and methane (C₁) are light hydrocarbons similar in size and polarities and thus difficult to achieve materials with favorable selectivities. Many forms of titanosilicate adsorbent demonstrated relevant C₂/C₁ selectivity that can be of interest for C₂ extraction through an adsorption process. Na-ETS-10 was particularly promise for the separation of C₂ from C₁. In the conventional extraction process, NG at high pressure (5000 kPa) is the feed stream of a distillation cryogenic process where it is split up in two main streams. A light stream (residue gas stream, RG) which is composed mostly by C₁ and a heavy stream (natural gas liquids, NGL) composed by C₂, C₃ and heavier hydrocarbons (Fig.1). A small fraction of C₂ slips with the RG stream and is eventually burned as fuel. It is estimated that several million barrels per day of C₂ are lost in this stream instead of being converted into other more valuable petrochemicals.

This work focuses on the design of an adsorption process to recover the small amount of C₂ slipping in the RG stream currently burned as fuel. The design work involves the simulation of adsorption cycles using computing codes considering rigorous mass, heat and momentum balances [1]. By taking into account the constraints associated with the energy consumption when the adsorption cycle is to be integrated into the conventional cryogenic process, a new cycle alternative was proposed which did not require recompression work for the C₁ stream. The cycle design uses a heavy reflux step at high pressure along with a pressure equalization step to achieve the targeted purities (Fig. 2). The process optimization in terms of purity and recovery helped to identify the best operating conditions.

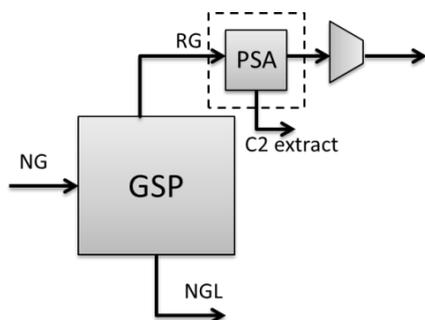


Fig. 1. Schematic of the Gas Subcooled Process (GSP) together with the PSA cycle

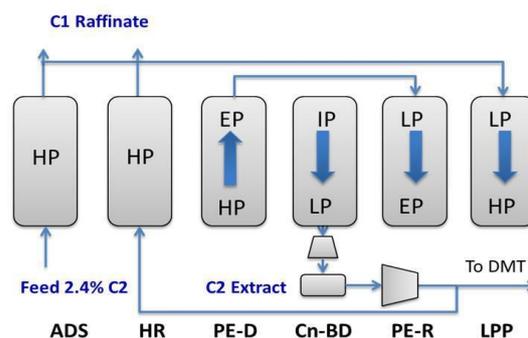


Fig. 2. Schematic of the proposed adsorption cycle to minimize recompression work.

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Multi-Scale Modeling and Simulation of All-Solid-State Sodium-Ion Batteries with Polymer-Ceramic Hybrid Electrolytes

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Lithium-ion batteries (LIBs) have been widely considered as the most promising power source for mobile devices. However, LIBs cannot meet the increasing global demand for electrochemical energy storage in the foreseeable future. Sodium ion-batteries (SIBs) are based on more ecofriendly and earth-abandoned materials. Commonly researched SIBs are based on liquid electrolytes. They pose leakage and thermal runaway risks. Solid polymer electrolytes solve these problems but need to operate at temperatures between 60-80°C to compensate insufficient ionic conductivity of polymer electrolytes at ambient temperatures.

We present a polymer-ceramic hybrid electrolyte which overcomes the necessity to operate at high temperatures. It combines the advantages of high ion-conducting solid ceramic particles and flexible polymers. Sodium metal serves as the anode and PEO with inorganic fillers is used as cathode electrolyte. Due to their sustainability and high efficiency—comparable to LIBs—sodium-ion batteries are a promising candidate for small scale stationary energy storage applications or mobile energy storage applications with less constraints regarding energy density (e.g. trains, ships, submarines etc.). This contribution highlights a modeling approach for simulations of a single battery cell to develop an optimal cell design of the aforementioned battery system. A newly developed multiscale modeling method for hybrid polymer-ceramic sodium ion batteries reflects the different length scales of the active particle level and the electrode level. We precisely describe the spatially resolved mass and charge transport as well as electrochemical reactions in the active particle and the surrounding electrolyte employing a finite volume method [1]. Both domains are resolved in 3D and the model framework was validated against experimental LIB data. The model output is incorporated in the connected pseudo-two-dimensional battery model for fast simulations of the overall battery cell considering mass and charge transport. The results support the importance of particle (active particle and ceramic filler particle) properties and configurations as well as electrolyte composition. In Addition, we present the evaluation of electrolyte properties with solid-state NMR spectroscopy and their model implementation. μ CT imaging experimentally investigates the cathode half-cell morphology. The derived virtual reconstructions enable realistic microstructure simulations of the battery cells. In this presentation, we will suggest two cell designs: The high-energy cell optimizes material efficiency and energy density. The high-power cell opts for high power densities (fast charging).

In summary, we present a novel all-solid-state polymer-ceramic hybrid sodium-ion battery type for small stationary or large mobile energy storage units. Our contribution outlines a simulation approach that sheds light on macroscopic and microscopic processes inside the battery-cell using a multiscale modeling method. As a result, a high-energy and a high-power design is derived.

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Evaluation of Hybrid Silica-Lignin Nanoparticles as Novel Additives for Water-Based Drilling Fluids

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Objectives

The general objective of this work is to evaluate the application of hybrid silica-lignin nanoparticles as viscosifier or filtration reducer additives in drilling fluids. It seeks to design fluids that emulate those used in drilling operations, especially in water-based formulations, whose use has grown in recent years due to the economic and environmental advantages they present compared to oil-based muds. This will allow delving into the possible technological variants that can be incorporated to replace high-cost components, currently imported in Argentina. Silica nanoparticles functionalized with sulfonated lignin are proposed as additives, and their effect on the main functional properties of fluids is compared to that of simple silica nanoparticles.

Materials and methods

Silica nanoparticles, both simple and functionalized with lignosulfonates were synthesized following a technique similar to that of Forchetti et al. [1]. Water-based muds were then prepared containing Na-bentonite, xanthan gum (XG), nanoparticles, and polyanionic cellulose (PAC). The concentration of the nanoparticles was varied in order to find the optimal formulation in terms of rheological behavior, filtration performance and temperature degradation. The obtained fluids were characterized in terms of: i) average diameter and morphological structure (by SEM), ii) rheological behavior (with a cone-plate rheometer), iii) filtration properties, and vi) ageing performance (with a rolling oven).

Results

The average diameters of the synthesized particles were 400 nm for the silica nanoparticles and 220 nm for the hybrid ones. Z-potential measurements showed -50 mV for the former and -32 mV for the latter, at a pH of 9. The prepared muds showed excellent performance in terms of rheological behavior, with a noticeable and desired pseudoplasticity. The filtration performance depended strongly on the concentration of nanoparticles, being always better with the hybrid particles. This seems to suggest that the lignin grafts play a better role in forming a good filtration cake than the silica particles alone. Thermal ageing showed expected results, corresponding to a loss of filtration performance and overall reduction of apparent viscosity. An optimal concentration of hybrid nanoparticles was found.

Conclusions

New water based muds for drilling operations were prepared. The use of lignin-functionalized nanoparticles showed promising results in terms of rheological and filtration performance. The partial or total replacement of traditional additives, such as xanthan gum, seems therefore possible. Further studies on this aspect are currently ongoing.

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Feasibility of FCC processability of VGO from Argentinian shale oil and a DCC approximation

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The current need for scientific and technical knowledge about the properties and processability of crude oils of non-conventional extraction source is driven by the growing demand of light olefins and middle distillates [1], as well as the sustained growth in the exploitation of non-conventional oil fields itself.

Given the reasons stated above, this paper compares the fluidized bed catalytic cracking (FCC) processing of two vacuum gas oils (VGO) from conventional (VGO_{ESC}) and non-conventional (VGO_{SOIL}) extraction crudes at two temperatures, 550 (typical of FCC) and 600 °C (an approximation to the deep catalytic cracking (DCC) technological option).

The experiments were performed in a laboratory batch fluidized bed reactor with internal recirculation, the CREC Riser Simulator [2]. An equilibrium catalyst of the gasoline maximization type, was used for the experiments. The feedstocks were obtained by the atmospheric and subsequent vacuum distillation in the laboratory of the respective crude oils to obtain the corresponding VGOs. The reaction products were analyzed by on-line gas chromatography (HP-1 column and FID detector). The coke on the catalyst was quantified by temperature programmed oxidation and subsequent methanation of carbon oxides. The conversion was defined as the sum of the mass yields of dry gas (DG, C1-C2), liquefied petroleum gas (LPG, C3-C4), gasoline (C5-216°C), light cycle oil (LCO, 216°C-340°C) and coke.

Both feedstocks showed similar conversions, except at low reaction times. At 550°C the conversions reached values of approximately 70% while at 600°C the conversions were almost 20% higher.

The comparison between feedstocks shows that the largest differences in the product yields were seen at 600°C. VGO_{SOIL} showed higher yields of gas products while higher yields of LCO were obtained with VGO_{ESC}. Regardless the feedstock, the gasoline yields were essentially the same. As both feedstocks have similar simulated distillation curves, the yield differences can be attributed to their different compositions. Coke yields were essentially the same with both feedstocks.

For each feedstock, at similar conversions, DG yields at 600°C doubled those at 550°C. LPG yields showed a small decrease with the temperature, but the olefinicity of the cut increased. Gasoline yield decreased with the temperature at similar conversions while LCO keep their values.

In conclusion, FCC processability of non-conventional VGO is possible under typical FCC conditions, with larger gases yields and the conservation of gasoline yields. More severe conditions, typical for DCC, induced good performances, with larger conversions, towards the production of higher amounts of light olefins, conserving gasoline yields and decreasing the yields of less valuable products, such as LCO.

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Sunflower husk roasting to improve the characteristics of biofuels

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Biomass can be considered an alternative to coal in the production of heat and electricity. Many types of biomass are waste from agriculture and the food industry. However, most agricultural and food waste have ash with a low melting point. This leads to a rapid growth of ash deposits on the heating surfaces of boilers; as a result, the real efficiency of boilers in which residues from agriculture and the food industry are burned is 45-50%.

The low melting point of ash is caused by the presence of alkali metal compounds in it [1]. To solve this problem, leaching of biowaste in water at a temperature of 80 – 240 °C is currently used. However, this biomass pre-treatment technology is complex and requires additional costs for drying the treated biomass.

We proposed to use torrefaction for pre-treatment of biomass, which increase the heat of combustion of biomass, increase the hydrophobicity of biomass, and reduce the cost of grinding it. In this paper, the characteristics of sunflower husk subjected to torrefaction by two different technologies are studied.

First, torrefaction in an environment of superheated steam at a temperature of 300 °C in fluidized bed reactor. Second, torrefaction in an environment of gaseous products at a temperature of 250 °C in hearth-type reactor. The resulting biochar has a calorific value of 14.8 – 23% higher than the initial husk. To assess the behavior of sunflower husk ash, predictive coefficients were calculated. Torrefaction of sunflower husks reduces slag formation probability by 2.31–7.27 times and reduces ash deposits probability on the convective heating surfaces of the boiler by 2.1–12.2 times. According to its fuel characteristics, the husk, after torrefaction in an environment of superheated steam, approaches wood waste, i.e. can be burned separately without additives or mixtures with other fuels with refractory ash. However, this type of torrefaction requires a large amount of energy to produce water steam, which increases the cost of the final product. In addition, the condensate formed after steam cooling requires disposal. It is proposed to carry out the torrefaction process in an intensively stirred bed in a heart-type reactor. Water mist is used to cool the biochar, which will also remove potassium and sodium compounds from the biomass. This will improve the fuel characteristics of the biomass.

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Production of a high carbon jet-fuel precursor from biomass derived furfural and 2-methylfuran using propylsulfonic SBA-15 catalysts

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According to the International Energy Agency, CO₂ emissions by cars, vans and trains will cease by 2050, but heavy trucks, maritime transport and aviation emissions will still be more than 0.5 Gt of CO₂. Therefore, it is imperative to develop routes for the production of biomass-derived C12-C15 molecules compatible with jet diesel. A C-C condensation process followed by hydrodeoxygenation (HDO) is required to achieve these biofuels. Among the alternatives, hydroxyalkylation-alkylation (HAA) reaction of furfural (FAL) and 2-methylfuran (2-MF) is the one of the best ones [1]. 2MF can be produced by a selective hydrodeoxygenation of FAL, which is obtained from nonedible biomass sources.

In this work, the synthesis of jet fuel range branched cycloalkanes oxygenated precursors by solvent-free HAA of FAL and its hydrodeoxygenated product, 2-MF, is explored. The catalysts employed were SBA-15 silica functionalized with propyl sulfonic groups. These mesoporous materials have structural and acid properties that can be tuned by adjusting syntheses conditions. We modified the amount of propyl sulfonic groups, the hydrophobicity of the catalyst and process conditions to optimize the production of the 15-carbon fuel precursor. The subsequent hydrodeoxygenation of the C15 molecule to paraffins was not studied in this work.

SBA-15 type silica was synthesized with 3 different loads of propyl sulfonic acid groups: 5, 10 and 15 mol%S/Si. The catalysts were labeled S5, S10 and S15 respectively. Loads greater than 15% were not used because a detriment in the ordering of the material was observed.

These catalysts were characterized and tested in solvent-free liquid reaction at a similar acid sites/F molar ratio and the same conditions. After each reaction test, the sample was diluted 500 times in acetonitrile and analyzed by gas chromatography with an MEGA-1 column and an FID detector. Catalyst S15 showed the best results. The optimal conditions found were: furfural conversion of 99.4% and C15 yield of 97.4% at 60°C after 2h of reaction with stoichiometric feeding of the pure reagents. In this case, a catalyst load of 0.7% of the total mass of reactants was employed. This value is compatible with the quantities used in the industry, indicating that this process is suitable to be scaled.

Nevertheless, it was observed that water in the feed highly affects the performance of the catalyst. For this reason, modifications were done on the hydrophobicity. A new catalyst was synthesized by the incorporation of hydrophobic groups by co-condensation. This catalyst was labeled as S15S+H. Catalysts S15 and S15B+H were tested at the same conditions. With the latter, a 14.5% improvement was obtained. Regarding selectivity, no significant differences were observed between both materials.

Finally, catalyst-recycling studies revealed that both catalysts, S15 and S15S+H, could be recycled 3 times with a minor reduction of activity.

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Uniform dispatch and storage of Green Hydrogen from wind energy in Patagonia Argentina. Cost impact.

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Green hydrogen is gaining wide acceptance in several countries in the world as an answer to a clean energy future. The focus of this study is to analyze uniform dispatch constraints and consequently the need for hydrogen storage. As it is known hydrogen storage is cost intensive because of the investment and energy consumption. Hence, the Levelized Cost Of Hydrogen (LCOH) production accounting for the whole system, wind farm, electrolyzer plant, and storage units, is addressed. In this study, three different scenarios according to different dispatch constraints and considering H₂ storage as compressed gas at 170 bar are investigated. A representative year is divided into several time-slots with equal lengths (number of days) and is modeled in hourly basis. A same amount of hydrogen must be dispatched for all the slots. The scenarios differ on the length of the time-slots. In the first scenario, the length of the time-slot is 1 day. This means that every day of the year the same amount of hydrogen calculated as the ratio of the total yearly production to the number of days must be dispatched. No constraints on the hourly H₂ production or dispatch within the slot are imposed. In the second scenario, the length of the time-slot is 7 days implying that a same amount of H₂ must be dispatched each week of the year. Similarly to the previous scenario, no constraints on the hourly production or dispatch within the slot are imposed. Finally, 14 days is assumed for the length of the time-slot in the third scenario.

For all of the scenarios, the minimum LCOH is obtained from the optimal combination of power peak of wind farm, power peak of electrolyzer plant and storage capacity. A model is implemented in EXCEL in order to determine the optimal system size for hydrogen production at minimum value of the LCOH including storage. It is shown that storage precludes the hydrogen annual production to reach the maximum value obtained when no storage is considered. In order to optimize the size of the entire process, the trade-offs among the hydrogen production (which depends on the length of the time-slot), storage capacity, seasonal changes in the wind resource should be taken into account. Hydrogen production is sacrificed in order to reduce the need for large Storage Capacity. Seasonal changes in the resource are the main reason for these behaviors. The optimization approach involves several heuristics rules that decide at each hour the amount of hydrogen the system produce. Hourly productions are constrained by different mathematical conditions, which are derived from mass balances.

Several suitable sites for hydrogen production with wind energy in South of Argentina are considered. A ranked list of the minimum values of LCOH computed for all scenarios and sites with H₂ storage is presented and the optimal behaviors of the subsystems (electrolyzer plant, wind farm and H₂ storage unit) are discussed in depth.



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Simplified conical tube network modeling for the characterization of gas diffusion layer

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Liquid water distribution within Gas Diffusion Layer (GDL) of a Polymer Electrolyte Membrane Fuel Cells (PEMFC) have a significant impact on the fluid-dynamic models of fuel cells or stacks and a simplified model to deal with it is still unknown. Other authors tackled this issue from different point of view: simulating the two-phase flow in porous media as a square lattice of tubes connected together at the nodes; dealing with the distribution of liquid water in the GDL of a PEM-FC through a Nano-scale Monte Carlo study; modeling a fibrous GDL as a regular cubic network of pore bodies and pore throats considering the size distributions.

A novel and simplified model for the characterization of the porous GDL in PEMFC is proposed. The porous structure is represented as a network of a set of interconnected truncated right circular cone tubes so-called as Conical Tube Network (CTN). Each component of the network is characterized by the small tube radius, the large tube radius, and the length and number of tubes. All these variables are obtained from the solution of a optimization problem minimizing the approximation error between Mercury Intrusion Porosimetry (MIP) experimental data and the model prediction. The main idea behind the model is the assumption that the CTN is filled during MIP experiments beginning from the large tube radius. In filling CTN, cumulative mercury volume intruded in the sample changes as a function of the tube radius. The geometry of this filling process is mathematically modeled. Experimental MIP results are represented as cumulative mercury volume as a function of the pore radius just intruded. For a given value of this experimental pore radius, tubes showing radius greater than the actual pore radius are completely filled, tubes with radius lower than de actual value are totally free, whereas tubes showing one radius greater than the experimental pore radius and the other lower than the experimental pore radius are partially filled in a fraction that can be computed. Optimization variables are length and number of tubes. Tubes radius are selected covering the range of experimental pore radius. However, resorting to discrete optimization, the set of tube radius is optimally selected. The maximum number of tubes radius is controlled with an upper bound constraint. The objective function to be minimized corresponds to the linear error between the cumulative tube volumes computed by the model and the experimental cumulative volumes obtained from MIP data. The equations of the model define a Mixed Integer Linear Programming (MILP) model. The characterization model is applied to a GDL 25BC from Sigracet. The model is implemented in General Algebraic Modeling System (GAMS) and it is solved with Gurobi solver.

A simplified set of 14 characteristic tubes radius is obtained resorting to optimization to describe accurately the cumulative volume distribution for the complete GDL. The cumulative volume distribution of the MIP experimental data is reproduced by mean of the CTN with a maximum relative error lower than 6.5% for the complete range of tube radius.



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Processing of symmetric ceramic multilayer by co-tape cast and co-sintering for SOFC/SOEC.

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Solid oxide cells are promising devices for energy conversion, with applications including chemical to electrical (fuel cell, SOFC) and electrical to chemical (electrolysis, SOEC). They are modular and compact allowing a wide range of applications [1]. In the electrolysis mode, the SOEC are attractive because of their electrical efficiency of steam conversion (H₂O) and the chance to capture carbon dioxide (CO₂) [2].

However, its commercialization is limited by the high cost of ceramic manufacturing. A way to sort it out is by reducing the number of steps and the temperature of the heat treatments required to fabricate the multi-component membrane electrode assembly (MEA) by co-tape and co-sintering process. In this sense, Tape-Casting is a well-established technique to produce thin ceramic sheets. It consists in extending a ceramic powder-based slurry along a surface and controlling the thickness with a "doctor blade". The green tape is dried and sintered to get the final layer of ceramic material. The cell components can be cast as a single multi-layer sheet and then laminated and sintered together to simplify the manufacturing process. However, this is the main challenge we face because of the coexistence of ceramics with different microstructural demands (porous electrode, dense electrolyte), which means different sintering temperatures that can produce shrinkage and chemical reactions between the component materials.

This research aims to investigate the processing of a symmetric multilayer electrode-supported button-cell for SOFC/SOEC by co-tape and co-sintering process. For this purpose, we develop a strategy for co-sintering. The structure studied is composed of SrTi_{0.3}Fe_{0.7}O_{3-δ}(STF) as the electrodes, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ}(LSGM) as the electrolyte, and La_{0.4}Ce_{0.6}O_{2-x}(LDC) as a buffer layer to prevent the chemical reaction between electrolyte and electrodes. In addition, Fe(III) as oxide was added to LSGM and LDC as a sintered aid, allowing us to decrease the sintering temperature of these components. Each tape was observed to ensure the absence of macro defects such as cracks or warps. The set of layers was laminated and cut and then the green multilayer was sintered at 1350°C by 12h. The sintered cell was analyzed by Scanning Electron Microscopy (SEM) to observe the microstructure and to verify the density and porosity of electrolyte and electrode, as well as to observe the interphases. The electrolyte density obtained is above 97% enough to avoid the passing of gases through it. The objective is to obtain a homogeneous interphase without macroscopic defects, to avoid the risk of layers being peeled off. The cation distribution through the cell was studied by SEM with energy dispersive spectroscopy (EDS) and by line-scan technique. It also would be further analyzed by TOF-SIMS. To study the performance of the cell, its current density was measured.

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Synthesis Of Pt/C Electrocatalyst at High Temperatures for PEM Fuel Cells Via Microwave-Assisted Polyol Method

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Proton-exchange membrane fuel cells (PEMFC) has attracted significant attention in the recent years, due to their wide range of applications. One of the main factors that determine the performance and cost of a PEMFC is the electrocatalyst used in the anode and cathode side. While Pt is the most used noble metal, its cost presents a significant restriction. Among the various electrocatalyst synthesis methods, polyol method offers a cost effective and easy way to synthesize carbon supported Pt electrocatalysts [1]. Polyol method offers a reasonable way to control the size and dispersion of Pt nanoparticles and microwave-assisted heating offers a uniform and efficient way of heating. Reaction temperature is one of the most important parameters for the synthesis of Pt nanoparticles but the maximum achievable reaction temperature is limited by the boiling point of the polyol mixture. By using a sealed reaction vessel, working at higher temperatures than the boiling point becomes possible. While the size of Pt nanoparticles can be controlled by reaction temperature, their dispersion and deposition on the porous carbon material can be affected by the pressure. Size control and dispersion of Pt can be optimized by control of these two parameters to provide alternative to the existing methods. This study focuses on the synthesis of Pt/C electrocatalyst at high temperature and pressure using microwave-assisted polyol method, to provide an alternative to the traditional polyol method using Hexachloroplatinic acid (Pt precursor), ethylene glycol (polyol) and Vulcan XC-72 (carbon support material). pH adjustments were done by using sodium hydroxide and hydrochloric acid. Reactions were carried out in completely sealed Teflon reaction vessel therefore allowing the polyol mixture to be heated above its boiling point. Heating was done using a variable power microwave synthesis unit. As the boiling point of polyol mixture is around 140 °C under normal conditions, catalyst synthesis reactions were carried out at 140, 160, 180 and 200 °C (Catalysts are denoted as Pt/C-T, where T is synthesis temperature) at 35 minutes reaction duration. All catalysts were filtered, washed using deionized water, and dried in an oven at 105 °C for 24 hours. Catalysts were characterized using BET (Brunauer–Emmett–Teller), SEM (Scanning electron microscope), FTIR (Fourier-transform infrared spectroscopy), XRD (X-Ray Diffraction) and CV (Cyclic Voltammetry). BET results show that surface area of 20% Pt/C-200 catalyst is 563 m²/g whereas commercial Vulcan XC-72 has a surface area of ~240 m²/g [2]. SEM imaging gives insight on how the surface morphology changes with synthesis temperature and FTIR spectroscopy shows the main chemical interactions on the surface of the catalyst. Crystallite sizes were determined according to XRD results as 1.95 nm for 140 °C and 13.20 nm for 200 °C. CV results show that electrochemical surface areas (ECSA) of Pt/C electrocatalysts are between 166.3 - 33.8 m²/g Pt (Pt/C-140 – Pt/C-200), where the maximum ECSA was achieved as 170.6 m² for Pt/C-160 catalyst. These results show that synthesis procedure used in this study provides an alternative method to conventional polyol process. Pt nanoparticles' formation speed, structure, size, shape, and deposition onto the porous carbon material can be influenced by temperature/pressure. By optimizing the reaction duration for various reaction temperatures and utilizing temperatures above 200 °C it may be possible to synthesize catalysts with higher ECSA and optimal crystallite sizes. More experimental work on this method is planned as well as experimental design studies. It is expected to provide more insight on optimization of Pt/C electrocatalyst synthesis using the microwave assisted polyol method.

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Understanding the differences in behavior between palm kernel shells and their structural components under pyrolysis conditions

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Biomass is an abundant resource that could support a transition from our oil-driven economy towards more sustainable alternatives. Among the different types of biomass, lignocellulosic residues emerge as one of the most promising feedstocks for obtaining fuels and platforms chemicals due to their potential to underpin the development of biorefineries, especially in industries with large waste generation [1]. Nonetheless, biomass seasonability and the variation of its thermal and physico-chemical properties, are main drawbacks for achieving continuous operations. Therefore, a detailed characterization of the residual biomass of interest, and a flexible technology to process such feedstock are required. Pyrolysis is a key technology for transforming residual biomass into valuable fuels and chemicals. However, for pyrolysis to be effectively scaled-up and incorporated into biorefineries, the complexity of the involved kinetic mechanisms and the interactions between its main components (cellulose, hemicellulose and lignin) need to be explored [2]. This work aims to provide information on the properties of palm kernel shells (PKS) with views to its later use for fuels and chemicals production via pyrolysis by exploring the differences in pyrolysis between PKS and its structural components. For this purpose, PKS are first characterized using proximal and elemental analysis. Cellulose, hemicellulose and lignin content in PKS is determined using high performance liquid chromatography and UV-Visible spectrophotometry. A synthetic mixture of cellulose, hemicellulose and lignin is also prepared to mimic PKS composition. The energy content of both the PKS and the synthetic mixture, is evaluated with the higher heating value (HHV). The pyrolysis of both PKS and the synthetic mixture is studied using thermogravimetric analysis (TGA) between 298-1073 K, using N₂ and with heating rates of 20, 35 and 50 K min⁻¹. The activation energy for the pyrolysis of PKS is determined using the Flynn-Wall-Ozawa model. The results evidence the existence of interactions between cellulose, hemicellulose, lignin and extractives in PKS pyrolysis. Moreover, under similar pyrolysis conditions, PKS showed higher gaseous and condensable products yields than the ones observed for the synthetic mixture. The activation energy for pyrolysis for the PKS varied between 116.41 and 137.07 KJ mol⁻¹, which is in accordance with the sample's high lignin (54.61 wt.%) and hemicellulose (25.65 wt.%) content. The differences between the studied samples are also shown in the resulting HHV, where 19.3 MJ kg⁻¹ and 17.5 MJ kg⁻¹ were obtained for the PKS and synthetic mixture correspondingly. This work constitutes a step forward in understanding the limitations that might arise when biomass is idealized as a mixture of pure components in complex processes such as pyrolysis.

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Hydrothermal liquefaction of sugarcane bagasse in the presence of catalyst and hydrogen donor at high heating rate to produce bio-oil with low-oxygen content.

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The production of biofuels from sugarcane bagasse has great potential due to its high hemicellulose and cellulose content. However, this biomass also has a high oxygen content, which reduces the calorific value of the biofuel obtained. Hydrothermal liquefaction (HTL) allows biomass to be thermochemically liquefied using hot, pressurized water (250-350 °C, 4-20 MPa) by taking advantage of the properties of water in a subcritical state. HTL at high heating rates allows rapid fractionation of biomass, decreasing the probability of re-polymerization reactions and lowering the residence times. The use of a basic catalyst (K_2CO_3) in HTL allows maximal conversion of lignocellulosic biomass to liquid products, leading to biofuels containing highly oxygenated compounds. The addition of ethanol (C_2H_6O) during HTL allows better contact between the reaction medium and the biomass, acting as a proton donor leading to radical stabilization and thus deoxygenation by dehydration of the liquid products [1][2]. In this project, HTL process was carried out in a stainless steel batch reactor (50 mL), where the parameters such as temperature (280, 300 and 320 °C), catalyst concentration (K_2CO_3 between 0, 0.5 and 1 M) and proton donor (Ethanol, 0-40 %v) were evaluated, while other parameters such as initial pressure (8 bar), heating rate (30 °C/min), reaction time (15 min) and biomass moisture (76 %p) were set. At the end of the reaction, the products hydrochar, bio-oil (heavier and two lighter fractions), and aqueous phase were separated. The HTL heavy bio-oil fraction impregnated in the hydrochar was recovered by Soxhlet extraction; the two lighter fractions were separated from the aqueous phase by liquid-liquid extraction with diethyl ether and ethyl acetate. Each of the bio-oil fractions were subsequently roto-evaporated and mixed. According to the results obtained from the HTL of sugarcane bagasse, the range of biomass conversion to liquid products varied between 94.4 - 67.9 %p, where the bio-oil yield was in the range between 47.0 - 17.4 %p. The oxygen content in bio-oil reached around 30.9 - 19.0 %p, where the calorific value was between 32.2 - 28.5 MJ/Kg, respectively. The best quality bio-oil was obtained at 320 °C, 1 M K_2CO_3 with proton donor. Under these conditions the process had a conversion to liquid products of 90.1 %p, 26.3 %p of bio-oil yield, 19.0 %p of oxygen in the bio-oil, and a calorific value of 32.2 MJ/kg. The combination of catalyst and proton donor allowed improving the HTL reaction due to the increase obtained in the conversion of biomass to liquid products and the production of a better-quality bio-oil by decreasing its oxygen content to 19.0 %p.

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Anaerobic Digestion of Agro-Industrial Wastewater with high sulfate rates: The issues of its reduction into sulphide and its consequences onto the biodigester's stability.

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The study of circular economy has brought attention to the potential use of agro-industrial wastewater as feedstock in fermentation or green chemical processes to produce new valuable products. When such strategies are not feasible, anaerobic digestion (AD) is the best alternative to convert stored chemical power into energy, while also avoiding the release of large amounts of organic matter into the environment. However, the presence of high sulfate levels in the substrate can hinder the application of AD by stimulating the growth of sulfate-reducing bacteria (SRB), which not only compete with other prokaryotes for substrates but also generate toxic levels of H₂S that affects methanogens and other microorganisms [1]. Hence, the generation of wastewater with high levels of sulfate and organic matter by several industries, including pulp and chemical plants, pharmaceuticals, and food processing facilities [2], emphasizes the need for greater attention and consideration.

In this experiment, the impact of high sulfate concentration in an agro-industrial wastewater (SS) on AD was investigated. Six independent anaerobic bioreactors were used, each with a 3-liter inoculum and designed to operate in semi-continuous mode. During the stabilization stage, the bioreactors were supplied with a constant volumetric organic loading rate (ORL, equal to 2g COD/liter.day) by providing a base effluent (BS) with a chemical oxygen demand (COD) of 200 g/l and negligible sulfate concentration. The feeding composition of the bioreactors was then modified by increasing the proportion of SS (a substrate with a COD of 100 g/l, pH of 4, and sulfate concentration of 25 g/l) while maintaining the ORL constant. Therefore, bioreactor R1: 100% BS = control; R2: BS 90% - SS 10%; R3: 70% BS - 30% SS; R4: 50% BS - 50% SS; R5: 30% BS - 70% SS; and R6: 100% SS.

The 50-day experiment evaluated several parameters, such as pH, production and quality of biogas (relative concentrations of CH₄, CO₂, O₂, and H₂S), sulfur balance, COD, etc. DNA extractions and metagenomic sequencing were conducted on the V3-V4 region of the 16S rRNA gene using the Illumina MiSeq platform. Results showed that an inhibitory process occurred as the proportion of SS increased, as evidenced by changes in the relative abundance of SBRs. Volatile sulfur compounds (VSCs) were observed when H₂S levels exceeded 10,000 ppmv, and MeSH, EtSH, and DMS were strongly correlated with SRBs, such as *Desulfocella*, *Desulfobacteraceae*, and *Desulfocarbo*. PICRUSt analysis also predicted an increase in the abundance of dissimilatory sulfate reduction enzymes. A significant decrease in the archaeal abundance and CH₄ production between bioreactors was noted: This could be due to the competition between methanogenic archaea and SRBs for substrates, as well as the heightened sensitivity of methanogens to H₂S toxicity.

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Effect of the presence of sediments on the distribution of hydrocarbons in an oil spill in freshwater

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Oil spills in freshwater generate short, medium, and long-term, adverse environmental effects. The mitigation of these impacts depends on the development and execution of good Contingency Plans, including identifying oil spill behavior and environmentally sensitive areas.

The oil spill behavior is usually predicted using numerical models, analyzing advection processes, mechanical dispersion, adhesion, evaporation, dissolution, vertical mixing, and resuspension. The transport processes (advection and dispersion) are evaluated using the Lagrangian method. The processes involved in the product's transformation and destination (water surface, atmosphere, water column, river or sea bottom, banks) are evaluated using numerical mass transfer models between the oil slick and the environment.

Studies have shown that the particles in the water column form aggregate with the oil, changing its buoyancy and final destination. However, the effect of factors such as mixing time and particle size has not been detailed studied. That is why this study mainly evaluated the hydrocarbons groups distribution in the water column after an oil spill in freshwater, in the presence of particles. In this case, a set of laboratory tests was carried out using heavy crude oil and three natural sediments mixed for 10, 120, 240, and 480 minutes. Additionally, tests without particles as references were used for every mixing time.

The particles were obtained from a sample of sediments collected from the Magdalena River -Colombia. The organic matter fraction of the sediments is 28% w/w, and the predominant mineral fraction is quartz, albite, and kaolinite. The particle-oil interaction test was performed based on the general baffled flask test (BFT) procedure of the United States Environmental Protection Agency -US EPA with minor modifications. The tests were carried out with five repetitions, following a factorial experimental design with the three particle size variations (> 38 μm , 125 – 250 μm , and 250 – 425 μm) and three mixing time variations (10, 240, and 480 min). Every experiment involves mixing 100 μl of oil with equivalent particles (p/p) in a baffled flask with 120 ml of distilled water, using an orbital rotator at 200 rpm. After mixing, the flask content was separated into three phases: floating (Phase A), submerged (Phase B), and settled (Phase C). The oil in every phase was extracted with dichloromethane, and its concentration was quantified using UV-Vis spectrometry. To evaluate differences in the groups of hydrocarbons per phase, the oil in dichloromethane solutions was analyzed by infrared spectroscopy and MALDI-TOF mass spectroscopy. The results reveal differences in the molecular weight distributions of hydrocarbons in the water column (floating, in the water column, or the bottom) in the presence of different sizes of particles and mixing time.

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Superior arsenic adsorption by growing iron oxide nanoparticles inside electrospun PVA nanofibers

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Introduction. Poly(vinyl alcohol) (PVA) is a hydrophilic and biodegradable polymer that has been electrospun to produce membranes containing iron oxide nanoparticles (IONPs) entrapped within polymeric nanofibers for arsenic adsorption from water. These membranes have severe limitations regarding scalability. In particular, the mass fraction of the adsorbent was limited to less than 3 wt.% and the nanofibers production rate was limited by the solution parameters. The incorporation of IONPs was performed either by synthesizing them in situ (by adding precursor salts and sodium hydroxide) or by suspending them in the electrospinning solution. [1, 2] Herein, a pristine PVA membrane was submerged in iron solutions and the growth of IONPs occurred by a second submersion in an alkaline solution. The objective of this work is to develop a novel production methodology to increase the arsenic adsorption capacity and production rate PVA membranes containing IONPs.

Material and Methods. A 12 wt.% PVA solution containing citric acid was prepared (5 wt.%/PVA) and electrospun (30 kV, 10 cm and 0.4 mL/h). Afterwards, the obtained mat was heat-treated to provide insolubility and then submerged in an iron solution. Three different iron solutions were tested (C1, C2, and C3), giving samples named PVA-C1, PVA-C2, and PVA-C3. C1 was prepared by dissolving 12 mg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 14 mg of FeCl_3 to 10 mL of water. C2 and C3 doubled and tripled the iron concentration of C1, respectively. All membranes were washed before characterization. Arsenic (V) adsorption was assessed via batch experiments by submerging 30 mg of samples in 10 mL having an initial concentration of 1100 $\mu\text{g/L}$ and pH 5 buffer. As(V) concentration was measured using the molybdenum blue method after 48 h.

Results. All membranes were self-supporting and stable in water, as revealed by SEM images. FTIR spectroscopy revealed that the predominant chemical structure is that of PVA for all the membranes. PVA-C1, PVA-C2, and PVA-C3 resulted in final concentrations of 106, 174 and 202 $\mu\text{g/L}$, respectively, giving adsorption capacities of 0.34 mg/g, 0.32 mg/g and 0.31 mg/g, respectively. Interestingly, the increase of precursor salts concentration reduced the adsorption capacity. This could be a consequence of bigger IONPs, with a consequent reduction in surface area.

Main conclusions. The proposed methodology triples the adsorption capacity reported for PVA membranes containing IONPs (0.34 mg/g vs 0.13 mg/g at 100 $\mu\text{g/L}$). [1] Moreover, the electrospinning rate of a PVA solution doubles that of iron oxide PVA containing IONPs (0.4 mL/h vs 0.3 mL/h), which is critical for escalation purposes.

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