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Plenary Lectures

PL1. Reactive crystal surfaces of metal-organic assemblies

Jorge A. Rodríguez Navarro^{1*}

¹ Departamento de Química Inorgánica, Universidad de Granada, Spain

* jarn@ugr.es

The reactivity of porous reticular materials such as metal-organic frameworks (MOFs) has been primarily understood in terms of processes occurring within their internal pores/channels. This approach has stimulated considerable research into engineering MOFs pore chemistry, allowing precise control over the chemical environment of their internal surfaces for targeted applications. This approach is effective for solid-gas processes with fully activated pores and small molecules, such as CO₂ or H₂O. However, their applicability can become limited in more complex systems, particularly those involving larger substrates or solid-liquid interfaces. In such environments, solvent molecules can partially or completely occupy the pore space, while diffusion and kinetic barriers restrict the access of reactants to the inner pore region. As a result, chemical transformations and adsorption events will mainly occur at or near the external crystal surface, rather than within the internal pore network (Figure 1).

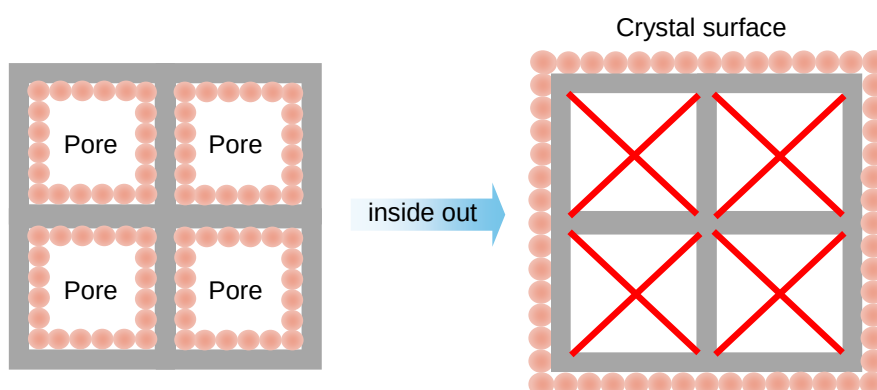


Figure 1. Pore nanospace vs. crystal surface. In reticulated porous materials, molecular interactions and reactions are governed by nanoscale confinement and diffusion within pores (see left), whereas exposed crystal facets provide direct, diffusion-free access to reactants without substrate size limitations (see right).

To exemplify this approach, I will show some examples of crystal surface reactivity of Zeolitic imidazolate frameworks (ZIFs) and metal-organic polyhedra polyoxometalate [MOP][POM] salts towards the selective break down of phosphoester and peptide bonds of biological and environmentally relevant substrates [1-5].

Acknowledgments

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PL2. New developments for 3D characterization of nanostructured materials by transmission electron microscopy

Sara Bals

EMAT and NanoLight, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp.

Sara.Bals@uantwerpen.be

Electron tomography (ET) is an outstanding technique for investigating nanomaterials in (scanning) transmission electron microscopy ((S)TEM). This technique is based on the acquisition of a series of 2D projection images, used as input for a 3D reconstruction algorithm. ET has been applied to determine the 3D structure and composition of metallic nanoparticles in great detail, even at atomic resolution [1,2]. There are however, still many challenges that require further progress.

Results

The time-consuming nature of conventional ET, makes it challenging to collect statistically representative data, necessary to establish structure-property connections. In addition to “fast” electron tomography, where we reduce the acquisition time for electron tomography from approximately 1 hour to a few minutes [3], we recently explored imaging by “secondary electron electron beam induced current” or “SEEBIC” as a route to high-throughput morphological quantification of chiral gold nanorods. SEEBIC enables a significant gain in data collection efficiency in comparison to conventional ET while providing necessary topographical information with superior resolution in comparison to scanning electron microscopy (Figure 1) [4,5].

Another challenge, which will be addressed in this talk, is related to the fact that 3D characterisation by TEM is typically performed using the conventional conditions of a TEM: ultrahigh vacuum and room temperature. We therefore combined dedicated in situ holders, providing more realistic environmental conditions, with optimised acquisition schemes, alignment procedures and 3D reconstruction algorithms. As such, we could investigate the organisation of ligands at the surface of nanoparticles and characterise the organisation of nanoparticles in an assembly in liquid. Moreover, the stability of gold nanoparticles, exposed to relevant environmental conditions, such as high temperature could be determined [6,7].

Finally, the talk will focus on the use of environmental gas TEM holders, based on MEMS devices, which has great potential since they enable significantly higher pressures in comparison to what can be reached using dedicated environmental TEM instruments. By combining aberration corrected electron microscopy with a quantitative interpretation and modelling approaches, we can perform quantitative measurements

of the coordination numbers of the surface atoms of catalytic nanoparticles at high temperatures and in gaseous environments [8,9].

Conclusions

The talk will focus on newest developments in the field of 3D characterization by TEM enabling the approach to be used to solve relevant problems in materials science.

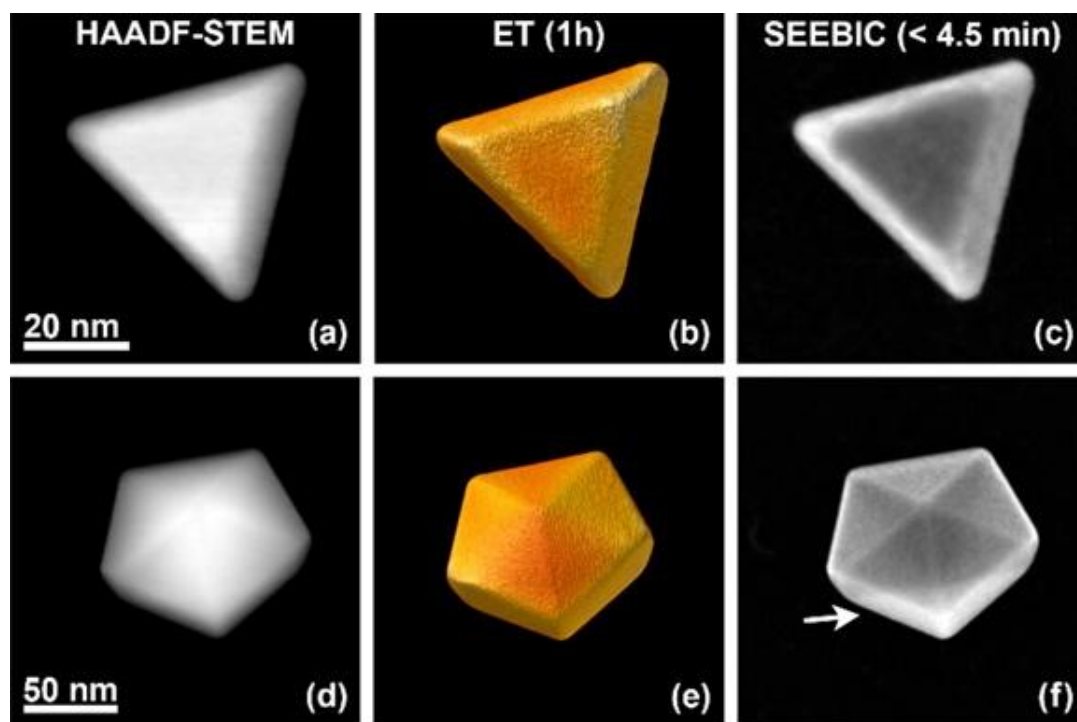


Figure 1. STEM images of an Au triangular platelet (a–c) and an Ino decahedron (d–f) obtained in different modes: (a, d) HAADF-STEM, (b, e) 3D surface visualization of an ET reconstruction, and (c, f) SEEBIC imaging. Reprinted from Ref. [4]

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PL3. Energy Harvesting and Storage Technologies on Flexible Platforms: From Multifunctional Building Blocks to Integrated Devices

Clara Rodrigues Pereira

¹ REQUIMTE/LAQV, Chemistry and Biochemistry Department, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

* clara.pereira@fc.up.pt

The transition towards clean and sustainable energy technologies, aligned with the goals of affordable and clean energy and responsible consumption and production, is driving the search for new materials and device concepts able to reduce dependence on conventional power sources. At the same time, the continuous development of portable, wearable and smart electronic technologies is creating new challenges for energy systems that must be lightweight, flexible, safe and easily integrated into non-conventional substrates. Flexible platforms, including textiles and plastic supports, offer unique opportunities to move energy harvesting and storage devices beyond rigid architectures, enabling new formats for autonomous and wearable-compatible technologies.

Supercapacitors stand out among flexible energy storage technologies due to their high power density, fast charge–discharge response, long cycle life and mechanical robustness [1]. Beyond conventional storage, the incorporation of additional functions within the same device architecture is opening new possibilities for smart and multifunctional systems. In particular, electrochromic and glow-in-the-dark textile supercapacitors combine charge storage with visual responses that may be explored for high-visibility safety apparel and real-time visualization of the charged/discharged state [2,3]. In parallel, thermally-chargeable supercapacitors provide a two-in-one approach by harvesting thermal energy from temperature differences between the human body and the surrounding environment, while storing the generated electrical energy for on-demand use [1,4]. Hybrid carbon/metal oxide-sulfide electrode nanomaterials and solid-gel polyelectrolytes have been key drivers of the advancement of these smart technologies.

This plenary lecture will provide an overview of our recent advances in the design of innovative flexible and wearable energy technologies [3–6]. The pathway from the tailored design and engineering of multifunctional building blocks to their deposition onto flexible textile and plastic substrates and assembly into versatile multi-tasking devices will be presented, using environmentally friendly and scalable methods across the different stages. The role of functional and hybrid carbon-based electrode nanomaterials and redox-active solid-gel polymeric electrolytes will be discussed by correlating their composition, structure, textural properties, redox activity, electrical

properties and substrate compatibility with the cooperative electrode/electrolyte interplay governing energy harvesting, electrochemical storage and optical response. Finally, the electrochemical performance, self-charging ability, upscaling potential and practical feasibility of the developed technologies for driving low-power electronics will be addressed.

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Keynotes

KN1. Watching CO₂ Inside Pores: Solid-State NMR as a Quantitative Window into Confined-Gas Adsorption

Luís Mafra*, Daniel Pereira, Márcio Soares, Pedro Ouro, Mariana Sardo, Ildefonso Marin-Montesinos, Mirtha Lourenço, Ricardo Vieira

Department of Chemistry & CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal.

* Imafra@ua.pt

Summary

An adsorption isotherm tells us how much CO₂ a sorbent holds, but not what the CO₂ has become. This talk centres on a solid-state NMR (ssNMR) strategy that, for the first time, decomposes an isotherm into its molecular constituents: in amine-functionalised mesoporous silica, six distinct ¹³CO₂ environments - three chemisorbed, three physisorbed - are individually quantified, independently modelled, and recombined into a total isotherm reproducing conventional manometry (0.81 vs 0.85 mmol/g), revealing that chemi- and physisorption contribute comparably across the pressure range [1]. Around this result, we show how ssNMR speciation, relaxometry and chemical-shift-anisotropy analysis, coupled to DFT and molecular simulation, expose the mechanisms governing CO₂ capture in amine-silicas, covalent organic frameworks, MOFs, carbon nitrides and biopolymer aerogels, and argue that molecular-level speciation, not bulk texture, should anchor sorbent design.

Introduction

Rational design of CO₂ sorbents is routinely guided by bulk textural descriptors (BET surface area, pore volume, total uptake), yet these metrics offer no direct insight into how CO₂ is chemically bound, nor why materials of similar porosity can differ sharply in selectivity or regeneration energy. Solid-state NMR (ssNMR) uniquely accesses this molecular-level information. In amine-grafted mesoporous silica (SBA-15), we first identified and structurally assigned three distinct chemisorbed carbamic acid/carbamate species ($\delta^{13}\text{C} \approx 153, 160, 164$ ppm) using ¹³C-labelled CO₂, two-dimensional heteronuclear correlation NMR and DFT modelling, establishing that CO₂ speciation depends on amine surface density and steric environment [2]. Chemical-shift-anisotropy (CSA) tensor analysis subsequently allowed us to unambiguously discriminate the neutral carbamic acid from the ionic alkylammonium carbamate ion pair, resolving a long-standing structural ambiguity and defining a threshold amine density (~ 1 molecule/nm²) above which proton transfer occurs [3]. We further showed

that trace pre-adsorbed water critically modulates this chemistry: it leaves primary-amine sorbents largely unaffected but boosts CO₂/CH₄ selectivity 36-fold in a tertiary-amine silica via a bicarbonate-forming pathway [4]. Building on this speciation framework, we developed a fully quantitative, ssNMR-assisted approach to construct entire CO₂ adsorption isotherms. That is the focus of this talk.

Main Results and Conclusions

In APTES-functionalised SBA-15, variable-pressure ¹³C multiple cross-polarisation combined with T1 relaxation measurements (up to 770 Torr ¹³CO₂) resolves six co-existing CO₂ environments: three chemisorbed species (A–C, δ¹³C 155–170 ppm, differing in hydrogen-bonding and ion-pairing state) and three physisorbed species (D–F, δ¹³C ≈ 125 ppm, distinguished purely by their molecular dynamics) [1]. Each population is quantified independently at every pressure point and fitted to its own Langmuir, Freundlich or Sips model; summing them reconstructs a total isotherm in close agreement with manometry (0.81 vs 0.85 mmol/g at 1 atm, 298 K; maximum capacity 1.5 mmol/g). Chemisorption and physisorption prove to contribute comparably throughout - six coupled processes that a volumetric measurement necessarily reports as a single curve.

This species- and dynamics-resolved approach generalises well beyond amine-silicas. In the covalent organic frameworks TpPa-1 and COF-42, variable-humidity T1 relaxometry separates three physisorbed CO₂ populations spanning three orders of magnitude in correlation time, showing that hydrophobic pores trap CO₂ in rigid, water-blocked configurations whereas hydrophilic pores segregate water and CO₂ far more cleanly — a molecular criterion for moisture tolerance under realistic flue-gas humidity [5]. In the industrially deployed MOF CALF-20, pressure-dependent CSA line-broadening uncovers a fluid-to-ordered transition of the adsorbed phase, driven by electrostatic templating between alternating framework charges and the CO₂ quadrupole moment; this couples to CO₂ but not to N₂, rationalising an outstanding selectivity that surface area alone cannot explain [6]. The same order-over-area principle recurs in sodium poly(heptazine imide), where in-plane crystallinity — not porosity — delivers uptake nearly double that of zeolite 13X at flue-gas temperature [7]. In cellulose and chitosan aerogels, amine density and residual structural scaffolding dictate whether physisorption alone or a mixed chemisorptive pathway operates [8]; a follow-up study converts this diagnosis into design, using aminosiloxane-grafted cellulose nanofibrils to shift uptake from purely physisorptive to >96% chemisorptive (3.1 mmol/g at 1 bar; ~2.0 mmol/g retained under humid direct-air-capture conditions) and to achieve the first ssNMR detection of CO₂ chemisorption directly from ambient air [9].

Taken together, these studies establish molecular-level CO₂ speciation and dynamics, accessed through quantitative ssNMR, as a design principle that supersedes bulk

textural metrics across chemically and structurally diverse sorbent classes, from amine-silicas to MOFs, carbon nitrides, biopolymers and waste-derived materials.

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KN2. Biogas upgrading in a multi-column VSA system using pelletized MOF

Esther Pancione¹, Francesco La Motta², Amedeo Lancia¹, Alessandro Erto^{1*}

¹ Department of Chemical, Materials and Industrial Production Engineering, University of Naples Federico II, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy (esther.pancione@unina.it, amedeo.lancia@unina.it, aleserto@unina.it).

² OILTECH srl, Via Lancetti, 43, 20158 Milano, Italy (f.lamotta@oiltech.it).

* Corresponding author: aleserto@unina.it

Pelletized Metal Organic Frameworks (MOFs) represent an emerging class of structured adsorbents for biogas upgrading, potentially combining high CO₂ affinity with fixed-bed processability. This work reports an application oriented experimental study of ProMOF 9100 for biogas upgrading by Vacuum Swing Adsorption (VSA) using a simulated biogas mixture containing 60 vol% CH₄ and 40 vol% CO₂. After preliminary single-column screening, the study focused on cyclic VSA operation in multi-column configurations. A four column VSA cycle achieved biomethane grade CH₄ purity of 97.3%, although with limited CH₄ recovery of 63.5%. Increasing cycle duration improved recovery up to 90.4%, but reduced purity to 85.2%. A five column cycle with one pressure equalization step was also tested as a comparison case. It increased CH₄ recovery and reduced energy consumption but caused a significant loss in CH₄ purity due to CO₂ slip. Therefore, the four-column configuration was identified as the most suitable option when product purity is prioritized.

Introduction

Biogas upgrading to biomethane requires the selective CO₂ removal from CH₄ rich streams while minimizing methane losses. Adsorption based processes, particularly Pressure or Vacuum Swing Adsorption (P/VSA), are attractive because they avoid chemical solvents, can be operated cyclically and are suitable for modular implementation. However, process performance is not governed only by equilibrium CO₂ capacity or ideal selectivity. Under cyclic operation, the adsorbent must also combine low CH₄ co-adsorption, sufficient working capacity and effective regeneration within realistic step times. Metal Organic Frameworks (MOFs) have been widely proposed for CO₂/CH₄ separation because of their tunable pore structure and strong affinity for CO₂. Nevertheless, many studies still focus on powders, equilibrium isotherms or model-based predictions. For industrial operation, MOFs must be available in a shaped form and validated under dynamic cyclic conditions [1,2]. In this context, the present work experimentally investigates a pelletized MOF in a laboratory scale multi-column VSA unit, linking adsorption behavior with process scale performance indicators.

Experimental

The adsorbent investigated was ProMOF 9100, commercially supplied by Promethean Particles Ltd. and based on a UTSA-16 family structure. Experiments were carried out in a laboratory scale VPSA unit equipped with five stainless steel columns, each with 30 mm internal diameter and 440 mm bed height. All tests were performed at 20 °C using a simulated biogas feed composed of 60 vol% CH₄ and 40 vol% CO₂ at 2.5 NL min⁻¹. Single-column tests were used as preliminary screening to define the cyclic operating conditions. Multi-column VSA experiments were then performed at 1 bar adsorption pressure and about 0.1 bar desorption pressure, without purge. Two configurations were investigated: a four column VSA cycle without pressure equalization and a five column VSA cycle with one pressure equalization step. Performance was evaluated at cyclic steady state in terms of CH₄ purity and recovery, productivity and specific energy consumption.

Results

Preliminary breakthrough experiments confirmed preferential CO₂ adsorption over CH₄ on ProMOF 9100. CH₄ always reached the column outlet before CO₂ and showed a roll-up associated with competitive displacement by the CO₂ adsorption front. The equilibrium CO₂ uptake increased from 2.41 mmol g⁻¹ at 1 bar to 3.27 mmol g⁻¹ at 8 bar, whereas CH₄ uptake remained below 0.4 mmol g⁻¹. These results confirmed the CO₂ selective character of the material, although mainly governed by competitive adsorption equilibrium rather than strict kinetic molecular sieving. Regeneration tests showed a long CO₂ release tail under vacuum. CH₄ purge accelerated the late desorption stage, but at the cost of methane consumption and losses; therefore, vacuum only regeneration was selected for the multi-column VSA tests. In the four column VSA configuration, a clear purity recovery trade-off was observed. Shorter cycle times preserved high CH₄ purity because adsorption was interrupted before significant CO₂ breakthrough, but methane recovery remained limited due to CH₄ retained in the bed and subsequently lost during evacuation. At 400 s total cycle time, the process achieved 97.3% CH₄ purity and 63.5% CH₄ recovery. Increasing the cycle time improved recovery up to 90.4%, but CH₄ purity decreased to 85.2% due to earlier CO₂ slip in the product stream. A representative compromise was obtained at 800 s, with 91.8% CH₄ purity, 89.6% CH₄ recovery, productivity of 3.6 mol h⁻¹ kg⁻¹ and specific energy consumption of 5.8 kJ mol⁻¹. The introduction of one pressure equalization step increased the maximum CH₄ recovery to 96.9% and reduced the specific energy consumption to 4.1 kJ mol⁻¹. However, this improvement was accompanied by a significant decrease in CH₄ purity, which ranged from 86.0% to 82.5%. This behavior suggests that, under incomplete regeneration, pressure equalization can perturb axial concentration profiles and promote CO₂ transfer toward the product end of the bed. Therefore, although the five-

column configuration improved recovery and energy performance, the four-column cycle was identified as the most suitable configuration when biomethane-grade purity is the primary target.

Conclusions

The pelletized MOF ProMOF 9100 showed clear CO₂ selectivity under simulated biogas conditions, but cyclic VSA performance was mainly controlled by regeneration kinetics rather than by adsorption capacity. Vacuum driven CO₂ desorption was characterized by a long tail, constraining the feasible ratio between desorption and adsorption times. Consequently, the process exhibited a strong trade-off between CH₄ purity and CH₄ recovery. Among the tested multi-column configurations, the four column VSA configuration was able to produce a CH₄ rich stream with biomethane grade purity, reaching 97.3% CH₄, but only at limited recovery. Extending the adsorption time increased CH₄ recovery but caused CO₂ contamination of the product. The five-column configuration with one pressure equalization step improved recovery and reduced energy consumption, but reduced CH₄ purity because of CO₂ slip. Overall, these results show that process level validation is essential when translating promising pelletized MOFs from material screening to realistic cyclic biogas upgrading. For ProMOF 9100, future improvement should focus on enhancing regeneration efficiency, optimizing pressure equalization strategy and controlling methane slip during evacuation.

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KN3. The VISION Spectrometer at ORNL: A Unique High-Throughput INS Platform for Materials Research

Anibal (Timmy) Ramirez-Cuesta

Oak Ridge National Laboratory (ORNL), Oak Ridge, TN, United States

Inelastic Neutron Scattering (INS) probes vibrational dynamics across the full energy range (0–4400 cm⁻¹) with exceptional sensitivity to hydrogen and light elements. By employing neutrons rather than photons, INS uniquely enables measurements under extreme conditions of pressure and temperature without requiring optically transparent windows, while providing direct insight into molecular mechanisms through comparison with computational models.

The VISION spectrometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory represents a transformative advance in INS instrumentation. It delivers unprecedented sensitivity and flux—up to two orders of magnitude greater than comparable instruments at low energy transfers—while seamlessly integrating three complementary techniques: vibrational spectroscopy (INS), structural characterization (neutron diffraction), and dynamical studies (quasielastic neutron scattering). This multi-modal capability creates a uniquely versatile platform for materials research.

A major recent breakthrough is the implementation of a high-throughput sample changer that enables analysis of 30+ samples per day, establishing VISION as the first high-throughput INS spectrometer. Combined with a newly established mail-in program, this capability dramatically expands access to neutron spectroscopy and enables systematic, large-scale materials screening previously impractical.

Applications exemplify VISION's distinctive capabilities in hydrogen-containing systems, particularly hydrogen storage in porous materials such as zeolites, carbons, and metal-organic frameworks (MOFs). INS measurements reveal short-range hydrogen–hydrogen interactions beyond the detection limits of conventional spectroscopies, rapid clathrate formation and molecular orientation in confined environments, and the emergence of super-dense hydrogen phases. The interplay between experimental INS data and atomistic modeling provides unprecedented mechanistic insight into molecular adsorption, confinement effects, and reactive processes—making VISION an essential tool for advancing hydrogen storage technologies, rational materials design, and fundamental understanding of confined-phase chemistry.

EXPERIMENTAL

The whole set of biomass samples were thoroughly **characterized** by Elemental Analysis (CHNS), Moisture, Ash and Volatile contents analysis, and Higher Heating Value (HHV) measurement. Once biomasses are considered fully understood, we are able to calculate and evaluate the **operation conditions** for further gasification experiments (temperature, stoichiometric ratio, biomass feed, gasification agent flow rate, and minimum fluidization velocity). A typical gasification experiment was performed at 900 °C, under 0,2 stoichiometric ratio, air flow rate ranging 1,5-2 L/min, and a biomass feed rate between 1-2 g/min (to operate at the required 2-5 u/u_m ratio). Prior to implementing an **extra gas adsorbent filter**, the same biomass sample (olive stone) was **pyrolyzed** at 900 °C, under CO₂ stream conditions. The obtained **biochar** was also texturally characterized.

RESULTS

The obtained gasification *syngas* is analysed by a microGC (*Figure 2.a*). After the addition of olive stones, Oxygen and Nitrogen concentrations drastically decrease to prepare the way to other gases (as **hydrocarbons**). With the **absence of oxygen** evidencing the success in the gasification, we just need to wait to stabilization.

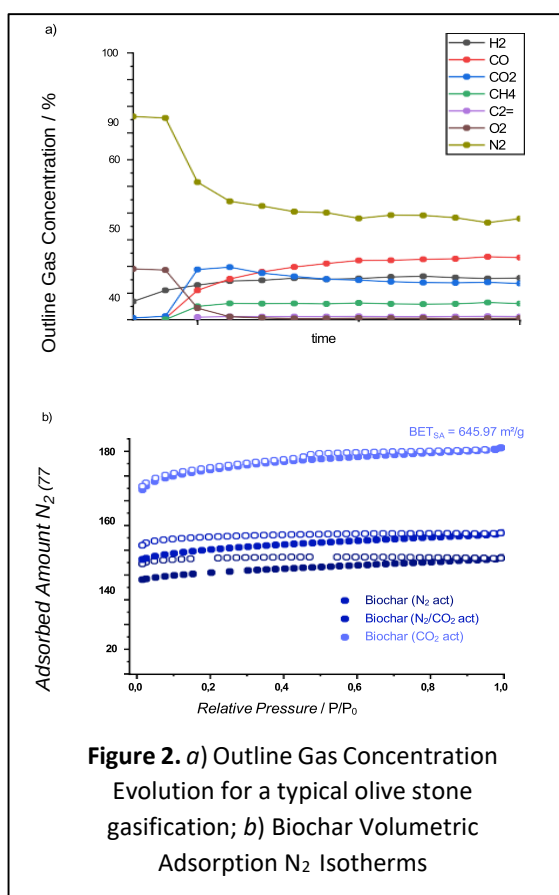


Figure 2. a) Outline Gas Concentration Evolution for a typical olive stone gasification; **b)** Biochar Volumetric Adsorption N₂ Isotherms

The observed **syngas composition** represents the typical gasification stream (H₂: 15-16%; CO: 23-24%; CO₂: 13-15%; CH₄(and other light HCs): 6-8%; with about 40% of N₂, as carrier gas, and main component of the gasification agent (air)). To assure process **reproducibility**, mandatory for further industrial implementation, each experiment has been replicated three times. Replicas' resemblance validates the operation method.

The preliminary results after the incorporation of the extra homemade **biochar-filter** in the outlet gas stream, exhibit a reduction in the carbon dioxide and ethylene concentrations in the *syngas*, corroborating (in addition to the biochar **adsorption isotherms** (*Figure 2.b*)) the indispensable role of this traditional, and inexpensive, adsorbent.

CONCLUSIONS

This promising strategy for mitigating **energy** future perspective is based on traditional **biomass gasification**, improved by the addition of a secondary biomass use, as biochar **adsorptive filter**. **Biomass** properties tune *syngas* composition, and **biomass biochar** enrich the gas outlet stream. This gasification **pilot-plant** smart-design promotes industrial **functionality** and **operativity**. “Shacking the Present, Shaping the Future”.

Acknowledgments

This work is part of the project “Synthesis of Advanced Biofuels by means of CCU approaches, combining new Catalytic Systems and Microreactors manufactured by 3D Printing (BIOCAS-CCU)”. The overall objective is to design, develop, and implement a circular technology for the synthesis of advanced biofuels from residual biomass, based on the combination of a gasification system, with a single-step catalytic system. The project is funded by MICIU (Ministerio de Ciencia, Innovación y Universidades, Spanish Government) in its Strategic Lines Projects Program (PLEC2024-011196; 2025–2028). The consortium is made up of 4 technological companies & 5 Spanish public institutions, constituting the perfect example of public-private collaboration. The authors thank Aragon Government and European Social Fund (GPT group, T22-2R).

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KN5. GAS-PHASE SIMULATED MOVING BED FOR METHANE UPGRADE

Rafael Dias^{1*}, Alexandre Ferreira¹, Alírio Rodrigues¹, Ana Mafalda Ribeiro¹

¹ LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

* rmdias@fe.up.pt

The main objective of this work was to develop a new and advanced adsorption process for methane and nitrogen separation based on the gas-phase simulated moving bed (SMB) technology. To do so, selecting the appropriate adsorbent and desorbent and studying its adsorption equilibrium and multi-component adsorption dynamics is vital to implement a mathematical model that can describe the system and effectively design the process. This way, a literature review on adsorbents and their performance for the herein studied separation was performed. Then, an SMB performance indicator (SPI) was developed to easily select the most efficient adsorbent/desorbent pair for a specific SMB application. Adsorption equilibrium isotherms and fixed bed tests were conducted for three carbon-based materials, and conventional gas-phase SMB processes were designed for each pair. Finally, a hybrid SMB/PSA process was proposed for separating equimolar CH₄/N₂ mixtures, removing the need for the desorbent in the process.

Introduction

The growing demand for natural gas has driven interest in unconventional methane which require the removal of impurities such as nitrogen. Due to the similar physicochemical properties between the two gases, N₂ is difficult to be removed and must be reduced below 3-4% to meet pipeline specifications. Industrially, this is accomplished by cryogenic distillation. While effective, this method is very energy-intensive and unsuitable for small to medium scale applications. As an alternative, adsorption-based methods offer lower energy consumption and scalability. However, their effectiveness is limited by low adsorption selectivity. SMB processes can overcome this limitation, enabling the separation of mixtures with selectivity close to unity, at almost isobaric and isothermal operation conditions.

Methodology

For each material, the adsorption equilibrium data of CH₄, N₂, CO₂, and Ar at 303 K, 323 K, and 343 K up to 2.5 bar was measured using a volumetric method. Both fixed-bed and SMB experiments were conducted at 303 K and 1.5 bar in the pilot gas-phase SMB unit. The *gPROMS* tool was used to perform all simulations, as well as design and model the hybrid SMB/PSA configuration.

Results

The SPI was formulated from the competitive CH₄/N₂ adsorption selectivity in the presence of the desorbent (CO₂), CH₄ uptake, and the heats of adsorption of both species, enabling the ranking of adsorbent/desorbent pairs from pure-component isotherms. Its predictive power was validated against separation region simulations for ten commercial adsorbents and extended to alternative desorbents (Ar) and to different applications (olefin/paraffin separation). The developed SPI is calculated with the following equation:

$$SPI = \frac{\alpha_{AB} \times q_A^2 \times \frac{\Delta H_A}{\Delta H_D}}{\frac{\Delta H_B}{\Delta H_D}} = \frac{\alpha_{AB} \times q_A^2}{\frac{\Delta H_B}{\Delta H_A}} \quad (1)$$

The performance of three carbon-based materials (commercial BPL activated carbon, in-house extruded Maxsorb pellets and in-house 3D-printed monoliths) was assessed for the separation of CH₄/N₂ mixtures by conventional gas-phase SMB using CO₂ and Ar as desorbent species. As an example, for the BPL activated carbon, isotherms show an adsorption strength order of CO₂>CH₄>N₂~Ar across the entire temperature and pressure range. Breakthrough tests validated the mathematical model and showed that both gases could effectively displace and be displaced by the CH₄/N₂ mixture. In SMB cyclic operation, complete separation was achieved with both desorbents, with Ar outperforming CO₂, producing 13.9 kg·m⁻³_{ads}·h⁻¹ of a methane stream with a 96.2% desorbent-free purity and 97.4% recovery. The internal profile at 50% of the switching time can be observed in Figure 1a.

The hybrid SMB/PSA process eliminates the need for a desorbent by replacing the regeneration zone with a PSA sequence (blowdown, purge, and pressurization), while the remaining columns operate in SMB mode, divided into a displacement zone and an adsorption zone. The feasible separation region (Figure 1b) was determined for purity targets of 97% CH₄ and 99% N₂, with analytical constraints derived for positive productivity of both streams. For the selected operation point, internal concentration profiles confirmed effective displacement and adsorption zone operation, producing average stream purities of 99% CH₄ and 99% N₂. Optimizing the purge flow rate and recovering part of the purge stream further improved recovery and productivity, up to 97.3 % and 11.5 kg/m³_{ads}/h. A low desorption pressure was required (0.1 bar), implying a power demand of 503 W·h·kg⁻¹_{CH₄}.

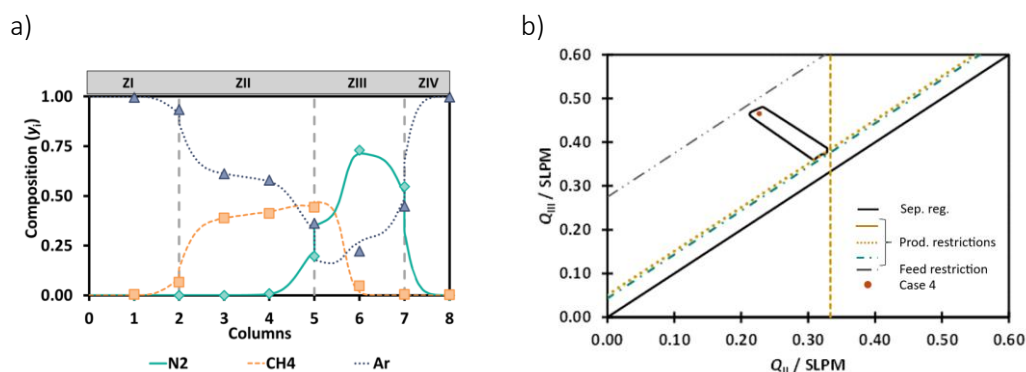


Figure 1 - a) Internal profile at 50% of the switching time for the SMB cycle using Ar as the desorbent and b) Hybrid SMB/PSA process separation region (full line). Dashed lines represent the derived constraints.

Conclusions

A novel SPI was developed to aid in the screening of adsorbent/desorbent pairs, validated for CH_4/N_2 and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separations. The first systematic experimental and computational study of a conventional gas-phase SMB for CH_4/N_2 separation was conducted across three adsorbent materials. Finally, an advanced desorbent-free hybrid SMB/PSA process was proposed and modelled, achieving >97% CH_4 purity and >97% recovery, competitive with state-of-the-art nitrogen rejection technologies for small-scale applications.

Acknowledgments

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Oral Communications

O1. Activated Carbons derived from Waste Biomass for CO₂ Capture and Biogas Upgrading

Julio E. Sosa ^{1*}, Brayan D. Batista ², Henry H. Ortiz ³, Edwin G. Fuentes ², Lluç Aresté-Saló ¹, Isaac J. Garcia ², Moisès Graells ¹, José P. B. Mota ³, Rui P. P. L. Ribeiro ³

*1*Department of Chemical Engineering (EQ), Escola d'Enginyeria de Barcelona Est (EEBE), Universitat Politècnica de Catalunya · BarcelonaTech (UPC), Campus Diagonal-Besòs, Av. Eduard Maristany, 16, 08019. Barcelona, Spain

2 Research on the Transformation of Industrial and Agro-industrial Matrices (ITMIA), Chemical Engineering Program, University of Cartagena, Piedra de Bolívar Campus, Avenida del Consulado, Calle 30 No. 48-152, ZIP Code 130015, Cartagena, Colombia.

3 LAQV REQUIMTE, Chemistry Department, NOVA School of Science and Technology |, NOVA FCT, 2829-516 Caparica, Portugal

* julio.eduardo.sosa@upc.edu

In this work, four activated carbons (SB1, SB2, SB3, SB4) were prepared from sugarcane bagasse (SB), a lowcost and widely available biomass residue, via urea doping and KOH activation. The use of this waste-derived precursor is motivated by the need for sustainable adsorbents for CO₂ capture, a key mitigation strategy against greenhouse gas emissions from fossil fuel combustion. The resulting materials exhibited controlled microporosity and modified surface chemistry. Adsorption equilibria of CO₂, CH₄, and N₂ were measured at 303 K Experimental data were fitted using the Toth model, while IAST was applied to predict multicomponent behavior. The materials exhibited competitive CO₂ adsorption performance compared with other biomass-derived activated carbons reported in the literature, which may be associated with enhanced porosity development and the introduction of oxygen- and nitrogen-containing functional groups during chemical activation. At low pressures, confinement in ultra micropores enhances CO₂ selectivity, whereas at high pressures pore filling dominates. Sample SB4 exhibited the highest selectivity, while SB1 showed the greatest adsorption capacity. Evaluation of adsorption metrics revealed a trade-off among selectivity, working capacity and regenerability.

Introduction

Greenhouse gases (GHGs) drive global climate change, with CO₂ contributing ~79% of emissions, mainly from fossil fuel combustion [1]. Its accumulation intensifies global warming, causing temperature rise, extreme events, and sea level increase, highlighting the need for effective mitigation strategies [1]. The European Union has reduced

emissions by 23% (1990–2018) and targets a 60% reduction by 2050 [1]. To this end, efficient CO₂ capture technologies are needed and, consequently, high performance porous materials [2]. Zeolites exhibit high adsorption capacity due to strong electrostatic interactions but are limited by high regeneration energy and moisture sensitivity [2]. Activated carbons (ACs) offer a low-cost alternative with high surface area and microporosity, where ultramicropores enhance CO₂ adsorption and surface chemistry influences selectivity (CO₂ > CH₄ > N₂). Biomass-derived ACs are particularly attractive due to their sustainability and low precursor cost, making waste-derived materials such as sugarcane bagasse a compelling choice [3].

In this work, activated carbons from sugarcane bagasse (SB) were synthesized, characterized, and evaluated for CO₂, CH₄, and N₂ adsorption. The Toth model and IAST were applied, and the potential for PSA/VSA performance was assessed using adsorption metrics to establish structure–property–process relationships.

Experimental

Four activated carbons were prepared from sugarcane bagasse biomass using different activation ratios. Adsorption equilibria were measured using a high-pressure magnetic suspension microbalance ISOSORP 2000 (Rubotherm GmbH, Bochum, Germany) [3]. The selectivity of binary mixtures was estimated using IAST, based on the parameters obtained from the pure components. Finally, all materials were compared using adsorbent selection criteria to evaluate their relative performance.

Results and Conclusions

The adsorption results show that all materials (SB1–SB4) exhibit fully reversible isotherms with no hysteresis, confirming that the process is dominated by physisorption and displays a clear pressure-dependent behavior (see Figure 1). At high pressures, the adsorption capacity follows the order SB1 > SB2 > SB3 > SB4, primarily controlled by surface area and total pore volume. In contrast, at low pressures, the order changes to SB1 > SB4 > SB3 > SB2, where adsorbent–adsorbate affinity becomes more significant. This effect is enhanced by the presence of oxygen- and nitrogen-containing functional groups introduced during chemical activation, which may contribute to stronger adsorbent–adsorbate interactions and improved adsorption performance. Overall, these results show that material performance depends directly on the interplay between pore structure and surface chemistry, both determined by activation conditions and sensitive to operating conditions.

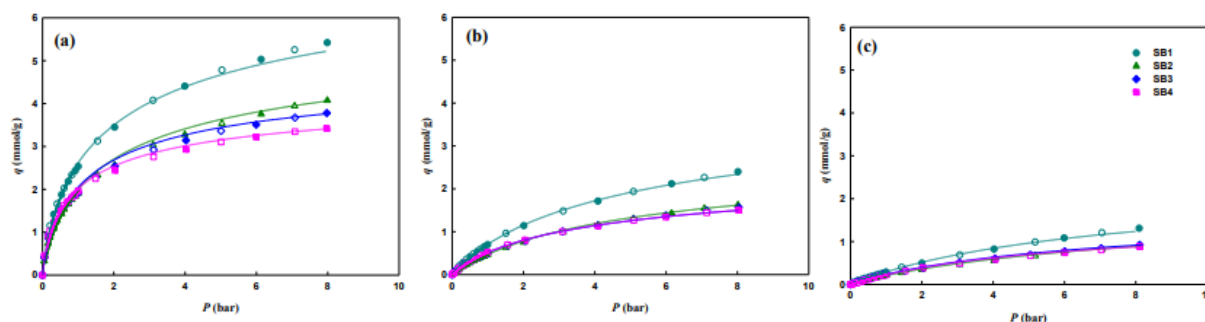


Figure 1. Adsorption equilibrium isotherms of: (a) CO₂, (b) CH₄ and (c) N₂ at 303 K and maximum pressure. Full symbols denote adsorption and empty symbols denote desorption data.

Acknowledgments

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O2. GRAPHITIC CARBON NITRIDE FOR Hg(II) ADSORPTION FROM AQUEOUS SYSTEMS

Amaya Arencibia^{1*}, Beatriz Villajos², Jorge Plaza², Carlos Márquez-Alvarez³, María José López-Muñoz^{2,4}

1 Dpto. Tecnol. Química, Energética y Mecánica, Univ. Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Spain.

2 Dpto. Tecnol Química y Ambiental, Univ. Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Spain.

3 Instituto de Catálisis y Petroleoquímica, ICP-CSIC, C/Marie Curie 2, 28049 Madrid, Spain.

4 Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS), Univ. Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Spain.

** e-mail: amaya.arencibia@urjc.es*

In this study, the potential use of graphitic carbon nitride materials (g-C₃N₄) as adsorbent of aqueous Hg(II) was explored. Bulk materials were synthesized from urea and melamine and further exfoliated to enhance porosity. Adsorption experiments using HgCl₂ solutions showed high removal capacity, reaching up to 108 mg g⁻¹. Performance was superior for urea based and exfoliated materials, correlating with improved textural properties and composition.

Introduction:

Graphitic carbon nitride (g-C₃N₄) is a metal free organic semiconductor prepared from s-triazine (poly-striazine) or s-heptazine (poly-s-heptazine) units bonded via secondary or tertiary amino groups. It is non-toxic, chemically and thermally stable up to 600°C, and exhibit a bandgap of 2.7 eV, that allows its use as photocatalyst under solar radiation [1]. However, it has also interesting properties for adsorption, because it can be prepared with suitable specific surface area, and, the surface is rich in amino groups, which provide active sites for adsorption of contaminants [2]. Moreover, it can be modified by exfoliation or by chemical reaction to increase the uptake capacity, which makes these materials interesting for adsorption studies. In this context, the performance of carbon nitrides as adsorbents of Hg(II) from aqueous systems has been studied, since it is a matter of great concern given the severe toxicity and bioaccumulative nature of mercury, even at trace levels.

Experimental:

In this work, g-C₃N₄ bulk was synthesized by thermal polycondensation of two precursors, urea (Bulk-U) and melamine (Bulk-M). The bulk samples were further

exfoliated by a thermal post-treatment at 450 and 500°C (Exf-U and Exf-M, respectively) to attain their exfoliation. The materials were characterized using XRD, N₂ adsorption–desorption isotherms at 77 K, scanning electron microscopy (SEM), FTIR and elemental analysis. Adsorption experiments were carried out to achieve equilibrium Hg(II) adsorption isotherms using aqueous HgCl₂ solutions ranging from 10 to 100 mg/L and an adsorbent dose of 0.25 g/L. Experiments were conducted using ultrapure water (UW) and water collected from the secondary effluent of a wastewater treatment plant (WWTP). Mercury concentrations were quantified by cold vapor atomic fluorescence spectrometry (CV-AFS).

Results and discussion

Results showed the strong influence of the precursor and the post-treatment on the physicochemical properties of the g-C₃N₄ materials and mercury removal (Table 1). Textural analysis yielded higher values of specific surface area and porosity for urea compared to melamine. Also, a clear enhancement of both parameters was achieved after the thermal exfoliation treatment, with the highest values corresponding to the Exf-U carbon nitride (99.4 m²/g and 0.27 cm³ g⁻¹). These higher values are related to the increment of the exfoliation degree, produced by the breaking of intralayer H-bonds and the interlayer stacking [1].

Table 1. Textural properties of synthesized g-C₃N₄ materials and Langmuir model parameters for Hg(II) adsorption in pure UW.

ADSORBENT	S _{BET} (m ² ·g ⁻¹)	V _p (cm ³ ·g ⁻¹)	Q ₀ (mg·g ⁻¹)	K (L·mg ⁻¹)
Bulk-M	8.8	0.02	59.7	0.14
Bulk-U	33.0	0.06	64.3	0.70
Exf-M	28.0	0.10	64.9	0.64
Exf-U	99.4	0.27	108	0.21

The Hg(II) adsorption was studied for all the materials by analysing the influence of water matrix, comparing the behaviour in the UW matrix and in the water matrix from WWTP, and the influence of pH. As an example, Table 1 displays the parameters estimated from Langmuir fitting of experimental mercury isotherms obtained in pure water at natural pH (~5). As can be seen, all the materials exhibit a notable adsorption capacity for Hg(II) removal from water, achieving values of up to 108 mg g⁻¹. Compared to the samples produced from melamine, those obtained from urea displayed a superior performance for Hg(II) uptake, showing Exf-U the best adsorption capacity. An

enhancement of adsorption capacity was produced after the exfoliation process. These results can be related to the different surface area, which is higher for the urea-derived samples and for exfoliated materials, but also elemental analysis could be taken into account. Similar effects were found for real WWTP, although, in this case, the Hg(II) uptake is generally lower due to the presence of other inorganic cations and anions, such as sodium, potassium, chloride, nitrates or sulphates, as well as organic species that interfere in the adsorption process due to competitiveness. Conclusion The synthesis precursor type and exfoliation of g-C₃N₄ play a significant role in its Hg(II) adsorption performance, which is mainly related with surface area. Although efficiency decreases in real wastewater matrices, these materials show potential as effective adsorbents for mercury removal from aqueous systems.

Acknowledgments

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O3. Tunable lignin derived carbon aerogels modified with ZSM-5 for hydrogen adsorption

J. Álvarez-Valcarce¹; A. Tabernero¹; S. J. Segovia-Sandoval²; V. Sebastian³; J. Silvestre-Albero²; J. Santamaría³; E. M. Martín del Valle^{1*}

1 Department of Chemical Engineering, University of Salamanca, Plaza de los Caídos s/n, 37001, Salamanca, Spain.

2 Department of Inorganic Chemistry - University Materials Institute, University of Alicante, Ctra. San Vicente – Alicante s/n, 03690, Alicante, Spain.

3 Department of Chemical Engineering, University of Zaragoza, and Nanoscience and Materials Institute of Aragon (INMA), 50018 Zaragoza, Spain.

** emvalle@usal.es*

The growing availability of lignocellulosic residues has driven increasing interest in their valorization for advanced material applications. In this work, lignin was employed as a renewable precursor for the production of activated carbons (ACs) with high specific surface area (SSA) for hydrogen storage. Lignin-based precursor hydrogels were synthesized and rheologically characterized using natural polysaccharides as polymeric matrices, into which ZSM-5 zeolite was incorporated to further enhance porosity and SSA. Following drying and KOH activation, hierarchical micro–mesoporous ACs with SSA values approaching 800 m² g⁻¹ were obtained. In several formulations, a direct relationship was observed between the viscoelastic properties of the precursor hydrogels and the SSA developed after activation. The resulting composites exhibited hydrogen adsorption capacities above 1 wt.% under atmospheric pressure conditions (5–6 mmol·g⁻¹). Further improvements in hydrogen uptake are anticipated through the incorporation of palladium nanoparticles, owing to the expected contribution of the spillover mechanism.

Introduction

The current global shift towards environmentally friendly energy sources has positioned hydrogen as a major alternative to fossil fuels. Hydrogen has great potential as a zero-emission fuel, although it does have certain drawbacks, such as the challenge presented by its storage. Consequently, in recent years, research has focused on developing porous materials capable of storing hydrogen through physisorption. In this regard, ACs are promising candidates as hydrogen storage materials due to their large SSA, lightness and high porosity. However, these materials are usually obtained through long synthesis processes, using organic solvents and without utilising materials considered to be waste.

Experimental

In accordance with what has been previously described, this study proposes the development of lignin based AC for hydrogen adsorption taking advantage of a biodegradable waste and natural polysaccharides as a polymeric network (by a synthesis process that avoids organic solvents, developed in previous work [1]), to provide a hydrogen storage system. In order to increase the SSA, a zeolite (ZSM-5) will be embedded into the polymeric network, leading to the development of novel AC composites. Furthermore, the potential relationship between the viscoelastic behaviour of the precursor (primarily the storage modulus related to the degree of crosslinking of the hydrogel) and the textural properties of the activated carbon (SSA) is evaluated.

The two selected polysaccharides have different gelling properties, gellan gum (GG) gels through thermal transitions, whilst alginate (Alg) gels through the use of CaCl_2 as a crosslinking agent. Both syntheses are performed in a single step, using water as solvent. These hydrogels will be characterised using oscillatory tests.

Subsequently, the precursor hydrogels will be freeze-dried to obtain the macroporous solid that will be activated. A preliminary carbonization step will be carried out prior to the chemical activation process. Both carbonization and chemical activation are conducted at $550\text{ }^\circ\text{C}$ during 30 min, with a heating ramp of $10\text{ }^\circ\text{C/min}$. Between these two stages, the carbonized solid will be immersed for at least 12 h in a 15 %w KOH solution to assure impregnation. The resulting ACs will be characterized by FTIR, FESEM, EDX, TGA and BET.

Results

Oscillatory tests confirmed that strong, stable precursor hydrogels were obtained for all concentrations used with both polysaccharides. The successful incorporation of ZSM-5 into the precursor hydrogel matrix, and its homogeneous dispersion, was confirmed by EDX and FTIR.

Chemical activation was performed successfully, reducing pore size from $150\text{--}500\text{ }\mu\text{m}$ to $2\text{--}5\text{ nm}$. Resulting ACs exhibited a wide range in terms of SSA (typical values of ACs obtained with other techniques), reaching maximum values of $763\text{ m}^2/\text{g}$ in the GG-Lignin-ZSM-5 composites and $790\text{ m}^2/\text{g}$ in the Alg-Lignin-ZSM-5 composites. Alg-Lignin-ZSM-5 composites exhibit a direct relationship between the storage modulus of the precursor hydrogels and the SSA, allowing a potential prediction of the SSA with a rheological analysis.

Once the ACs with the highest SSA had been found, their hydrogen adsorption capacity was measured, with all of them exceeding 1 wt.% at cryogenic temperatures and atmospheric pressure. As this hydrogen adsorption value is still below our targets, the aim is to increase it by spillover effect induced by palladium nanoparticles. In a subsequent step, Pd nanoparticles will be embedded in the same way as ZSM-5 into the precursor hydrogel polymeric network. Conclusions Lignin based ACs have been successfully developed with SSAs of over 750 m² /g. These composites use natural polysaccharides to form a polymeric network which supports both, lignin and ZSM-5. It has been demonstrated that the crosslinking method and the viscoelastic properties of the precursor hydrogel can be modified to control the SSA. In fact, a higher storage modulus generally implies a higher degree of crosslinking, increasing the SSA. These materials have been used for hydrogen adsorption exceeding 1 wt.%.

Acknowledgments

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O4. Textural Characterisation of Porous Carbons from Pig Hair biowastes Using N₂, O₂, and CO₂ Adsorption

Kiara Montiel-Centeno, Jose Villajos, José María Sánchez, Ignacio Campello, Cristina Gutiérrez*

Hydrogen and Power-to-X Department, Iberian Centre for Research in Energy Storage (CIIE), 10003 Cáceres, Spain.

**cristina.gutierrez@ciie.org*

Abstract

Porous carbons were synthesised from pig hair biowaste, a keratin-rich underutilised by-product, by mechanochemical-assisted K₂CO₃ activation and characterised using N₂, O₂, and CO₂ adsorption. Increasing the K₂CO₃ content enhanced porosity, yielding surface areas up to 3500 m² g⁻¹. Compared with N₂ adsorption, O₂ adsorption yielded systematically higher textural parameters, suggesting enhanced accessibility to narrow micropores that may be partially diffusion-restricted for N₂ at 77 K. The combined use of N₂, O₂, and CO₂ enabled a more comprehensive assessment of pore accessibility and porosity development, offering a more robust framework for evaluating porosity development in highly microporous carbons derived from animal biomass residues.

Introduction

Porous carbons derived from biomass have attracted considerable attention due to their high surface area, tunable pore structure, and potential applications in adsorption, gas storage, and environmental remediation [1,2]. Among the numerous biomass residues, pig hair waste is an abundant keratin-rich by-product of the swine-processing industry whose valorisation as a carbon source remains relatively unexplored [2]. The characterisation of highly microporous carbons nevertheless requires careful consideration, since the textural properties of porous carbons strongly depend on the probe molecule employed and on diffusional limitations within narrow micropores [3]. Therefore, in this work, porous carbons were produced from pig hair biowastes through a mechanochemical-assisted K₂CO₃ activation route and comparatively characterised by N₂ and O₂ adsorption at 77 K and CO₂ adsorption at 273 K.

Experimental

Porous carbons were produced from pig hair via a mechanochemical-assisted K₂CO₃ activation route. Pig hair and K₂CO₃ were mixed at mass ratios of 100:0 (PHC), 90:10, 75:25, and 50:50 and milled at 30 Hz for 60 min in a Retsch mixer mill using a 50 mL

milling jar and five 10 mm milling balls. The mixtures were subsequently carbonised at 900 °C for 2 h under N₂ flow (120 mL min⁻¹) at a heating rate of 3 °C/min. The resulting carbons were washed with 1 M HCl, rinsed to neutral pH, and dried at 80 °C for 12 h. Textural properties were determined from N₂ and O₂ adsorption isotherms at 77 K and CO₂ adsorption isotherms at 273 K using a 3Flex sorption analyser after degassing the samples at 200 °C for 12 h under vacuum.

Results and discussion

Figure 1 shows the N₂ and O₂ adsorption isotherms measured at 77 K for porous carbons synthesised from pig hair using different K₂CO₃ contents. The control sample (PHC) exhibited negligible adsorption capacity, whereas increasing the K₂CO₃ content progressively promoted pore development. The N₂ adsorption isotherms of PHC-75:25 and PHC-50:50 showed a steep uptake at low relative pressures ($p/p_0 < 0.1$), characteristic of Type I isotherms and indicative of predominantly microporous structure [3]. In addition, PHC50:50 showed adsorption at intermediate and high relative pressures, suggesting the development of mesoporosity. Accordingly, the specific surface area increased markedly from 20 m²/g for PHC to 2180 and 3050 m²/g for PHC-75:25 and PHC-50:50, respectively, while the total pore volume increased from 0.02 to 2.13 cm³/g.

The comparison between N₂, O₂, and CO₂ highlights the complementary information provided by each probe molecule. O₂ systematically yielded higher surface areas and micropore volumes than N₂, suggesting enhanced access to narrow micropores where N₂ diffusion may be limited. This behaviour was particularly evident for PHC-90:10, for which the micropore volume obtained from CO₂ adsorption was 0.16 cm³/g, exceeding the total pore volume determined by N₂ adsorption (0.09 cm³/g) and closely matched that obtained from O₂ (0.15 cm³/g). This result indicates that PHC-90:10 contains a substantial content of very narrow micropores, which are more effectively probed by O₂ and CO₂. In contrast, the lower micropore volumes estimated from CO₂ adsorption for PHC-75:25 and PHC-50:50 suggest that, in these highly activated samples, CO₂ preferentially probes the narrowest and most energetically favourable micropores, whereas N₂ and O₂ characterise a broader fraction of the porous network. Overall, the combined use of N₂, O₂, and CO₂ adsorption revealed a progressive evolution of the pore system with increasing K₂CO₃ content. PHC90:10 was dominated by ultramicropores accessible to O₂ and CO₂ but only partially detected by N₂, whereas PHC-75:25 and PHC-50:50 exhibited increasingly developed micro- and mesoporous networks. Among the investigated materials, PHC-50:50 exhibited the highest surface area and pore volume, indicating a strong influence of the activating agent content on pore development and accessibility.

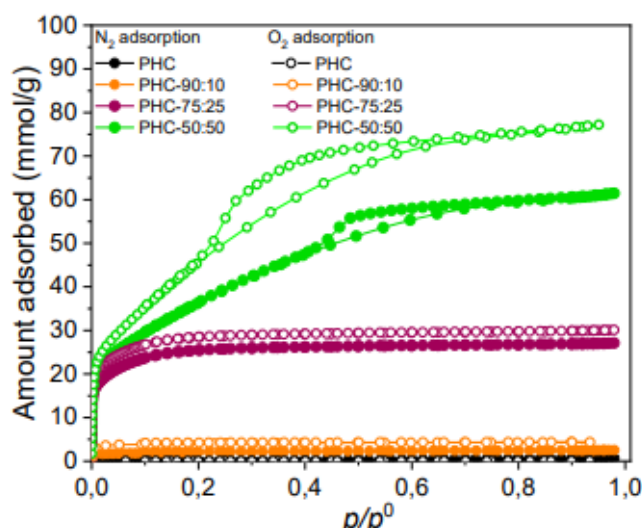


Figure 1. N₂ and O₂ adsorption–desorption isotherms at 77 K of PHC materials.

Table 1. Textural properties of PHC determined from N₂ (77 K), O₂ (77 K), and CO₂ (273 K) adsorption isotherms.

Sample	$S_{\text{BET}}/\text{N}_2$ (m ² /g)	$S_{\text{BET}}/\text{O}_2$ (m ² /g)	V_{TP}/N_2 (cm ³ /g)	V_{TP}/O_2 (cm ³ /g)	$V_{\mu\text{P-}\alpha}/\text{N}_2$ (cm ³ /g)	$V_{\mu\text{P-}\alpha}/\text{O}_2$ (cm ³ /g)	$V_{\mu\text{P-DR}}/\text{CO}_2$ (cm ³ /g)	V_{MP}/N_2 (cm ³ /g)	V_{MP}/O_2 (cm ³ /g)
PHC	20	0	0.02	0	0.02	0	0.02	0	0
PHC-90:10	160	300	0.09	0.15	0.06	0.13	0.16	0.03	0.02
PHC-75:25	2180	2450	0.94	1.04	0.85	0.95	0.36	0.09	0.09
PHC-50:50	3050	3500	2.13	2.67	1.28	1.71	0.26	0.85	0.96

Conclusions

K₂CO₃ activation effectively promoted pore development in pig hair-derived carbons, with increasing activating-agent content leading to a progressive enhancement of the porous structure. O₂ adsorption yielded systematically higher micropore volumes than N₂, indicating improved access to narrow micropores, while CO₂ provided complementary information on the most confined microporous domains. The combined use of these probe molecules enabled a more comprehensive assessment of pore accessibility and porosity evolution.

Acknowledgments

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05. DESIGN OF A PRESSURE-TEMPERATURE SWING ADSORPTION PROCESS FOR METHANE UPGRADE

Mariana C. N. Bessa^{1*}, Idelfonso B. R. Nogueira², Alexandre F. P. Ferreira¹, Alírio E. Rodrigues¹, Ana Mafalda Ribeiro¹

¹ LSRE-LCM, ALICE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

² Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim 7034, Norway

* e-mail of the main author: up201503607@edu.fe.up.pt

The main objective of this work is to design and simulate an industrial-scale PTSA (Pressure-Temperature Swing Adsorption) process and assess whether it can replace an existing multicolumn cryogenic distillation process for LNG (Liquefied Natural Gas) production, in which the CO₂ content must be below 50 ppm. The novelty of this work lies in the development and implementation of a new methodology for designing an adsorption process that produces high-purity CH₄ at temperatures below 210 K, which includes the use of symbolic regression to generate Surface Equations (SEs) that fit the thermodynamic properties given by the GERG-2008 Equation of State (EoS), which accounts for deviation from ideal gas behavior accurately. The derived SEs from the GERG-2008 EoS data are used to describe thermodynamic properties, thus reducing simulations' CPU time.

Introduction

Natural gas has emerged over the past two decades as a promising fuel to replace coal and oil worldwide. It consists of CH₄ (typically 87-97%), heavier hydrocarbons, CO₂, He, H₂S, and N₂. Natural gas upgrading is an essential step before transport, removing impurities such as CO₂ and N₂ to enhance the fuel's energy content and prevent corrosion in pipelines and equipment. The presence of CO₂ (above 50 ppm) in LNG plants poses a major problem, as it can form dry ice inside pipeline networks. Therefore, the separation of CO₂ from natural gas streams is vital. Cyclic adsorption processes, particularly PTSA, under nearly cryogenic conditions have been proposed as a cost-effective alternative for producing high-purity LNG, owing to their lower energy consumption and reduced operating costs. Among the available adsorbents for CO₂/CH₄ separation, binderless 13X zeolite is notable for its high thermal stability and surface area.

Methods

The single-component adsorption equilibrium isotherms for CO₂ and CH₄ on binderless 13X zeolite beads were measured and fitted to the DSL (Dual-Site Langmuir) model with good accuracy by a previous study from our research group [1]. The dynamic behavior of adsorption for the PTSA process was represented by a phenomenological model that includes mass, energy, and momentum balances. Under specific pressure and temperature conditions, the gas phase cannot be considered ideal; thus, the gas thermal properties can be more accurately predicted using SEs based on the values obtained with GERG-2008 EoS in the NIST REFPROP (REfERENCE fluid PROPERTIES) software package. The GERG-2008 EoS values were fitted to SEs using the symbolic regression method in the PySRRegressor library in Spyder (Python), with genetic programming (GP) as the search algorithm, and were subsequently incorporated into the phenomenological model. This method generates various candidate mathematical models in successive generations for representing the nonlinearity in the input-output relationship and identifies the overall top-performing SE based on the error between the input/"true" values (in this case, the GERG-2008 EoS values) and the output/predictive values. Breakthrough curve simulations were conducted to comprehend the dynamic behavior of adsorption/desorption throughout the packed columns, and the PTSA process was then simulated until a cyclic steady state was reached.

Results

The developed SEs are valid for CO₂/CH₄ gas mixtures at temperatures between 180 and 650 K, pressures from 0.1 to 45 bar, and CH₄ molar fractions between 65% and 100%. The values calculated with the SEs present average relative errors of 0.07%, 1.0%, 0.54%, 0.84%, and 0.62% for the compressibility factor, heat capacities at constant pressure and volume, density, and viscosity, respectively. The maximum relative errors were 5.1%, 8.4%, 9.9%, 7.5%, and 7.9% in that same order of properties. Thus, the values determined by the SEs are in good agreement with the ones obtained using the GERG-2008 EoS. The PTSA process for replacing the final two distillation

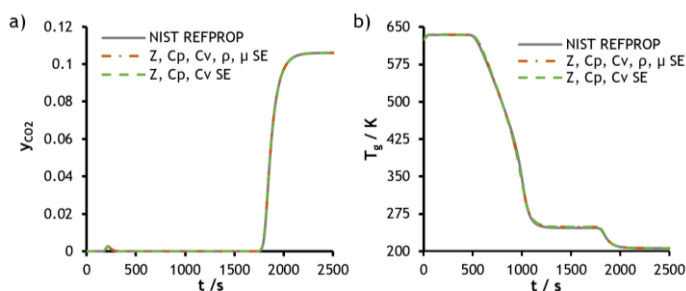


Figure 1 – Breakthrough curve for the adsorption step.

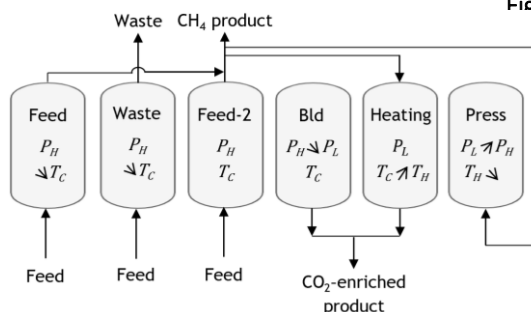


Figure 2 – PTSA cycle.

viscosity, respectively. The maximum relative errors were 5.1%, 8.4%, 9.9%, 7.5%, and 7.9% in that same order of properties. Thus, the values determined by the SEs are in good agreement with the ones obtained using the GERG-2008 EoS. The PTSA process for replacing the final two distillation

columns in the Berstad et al. [2] plant is supplied with a gas stream at about 3185 mol s^{-1} containing 10.6% CO_2 and 89.4% CH_4 . It was considered that the PTSA process would consist of two parallel, equal units, each fed with 1593 mol s^{-1} . First, breakthrough curve simulations for the adsorption (co-pressurization with 50 ppm CO_2 followed by the feed step) and heating steps were run for three thermodynamic calculation methods (REFPROP-GERG-2008 EoS and two cases with SEs from this work). The breakthrough curve simulations for the adsorption step are presented in **Figure 1**. A PTSA cycle composed of the following steps was simulated: feed, waste, feed-2, blowdown, heating, and pressurization (see **Figure 2**). The proposed cycle design produces methane with 46.2 ppm CO_2 , with a recovery of around 43.2% (compared with 70% for the last two columns of the cryogenic distillation).

Conclusions

The simulation results for the PTSA process, using the developed SEs, show that the proposed cycle produces methane that meets the LNG CO_2 content specification (<50 ppm) and achieves a recovery of around 43.2%.

Acknowledgments

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O6. LIQUID-PHASE ADSORPTION OF XYLENES USING A BARIUM-POTASSIUM EXCHANGED FAUJASITE ZEOLITE

Bruno Castro^{1*}, Rui Faria², Jonathan Gonçalves², Alírio Rodrigues¹, Alexandre Ferreira¹

¹ LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

² Currently at Bondalti Chemicals, Rua do Amoníaco Português nº 10, 3860-680 Estarreja.

* up201505452@up.pt

The main objective of this work is to develop a Simulated Moving Bed Reactor process to produce *p*-xylene, using a hybrid bed composed of both the adsorbent and the catalyst, to maximize the conversion of isomers and the selectivity towards *p*-xylene. The separation of *p*-xylene by adsorption decreases its concentration in the liquid medium, allowing the isomerization of *o*- and *m*-xylenes to go beyond the thermodynamic equilibrium, further increasing the production of this isomer. The first part, presented here, is related to adsorption, where a FAU-type zeolite exchanged with barium and potassium was used. This zeolite shows greater affinity for *p*-xylene than toluene, *o*-xylene and *m*-xylene, which demonstrates it is a suitable adsorbent to mix with the catalyst to create the hybrid bed.

Introduction

Xylenes (ortho, meta, and para) are valuable chemicals used in various industries, such as petrochemical, pharmaceutical, and manufacturing sectors. However, due to their similar physical properties, it is difficult to produce the isolated isomers with a high degree of purity. *p*-Xylene is the most valuable isomer and can be recovered from the other isomers by selective adsorption in fixed bed columns using the concept of Simulated Moving Bed (SMB). The adsorbent used in a SMB unit needs to be thermal, mechanical, and chemically stable, as well as have an adequate adsorptive capacity and be capable of taking advantage of molecular differences between several constituents of the mixture. A faujasite-type zeolite exchanged with barium and potassium was used to separate these compounds.

Experimental

The adsorbent was first subjected to an ion exchange step to replace the sodium (Na⁺) cations, initially present in the zeolite, with barium (Ba²⁺) and potassium (K⁺) cations through contact with a solution containing 1.0 M of barium chloride and 0.3 M of potassium chloride. X-ray Photoelectron Spectroscopy (XPS) analysis shows that the degree of exchange is very high, with only 4.2 % of the sites occupied with sodium, therefore demonstrating the efficiency of the applied treatment. Regarding the effects

of the ion exchange steps on the structure of the material, the results indicate that no significant structural changes occurred, as the $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.06$ remained very close to the value reported by the manufacturer ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$).

The adsorption isotherms for each component were determined through breakthrough curves in a fixed bed column. The Dual-Site Langmuir mathematical model was used to describe the experimental data and the results are presented in Figure 1 and Table 1.

Results and Discussion

The adsorption equilibrium data for *o*-xylene, *m*-xylene, *p*-xylene and toluene, obtained from the breakthrough curves show a good fitting between the experimental and calculated data, thereby validating the proposed mathematical model. The barium and potassium exchanged faujasite presents similar saturation capacities for all xylenes, while for toluene, the saturation capacity is slightly higher. However, the affinity towards each site differs significantly between the different adsorbates.

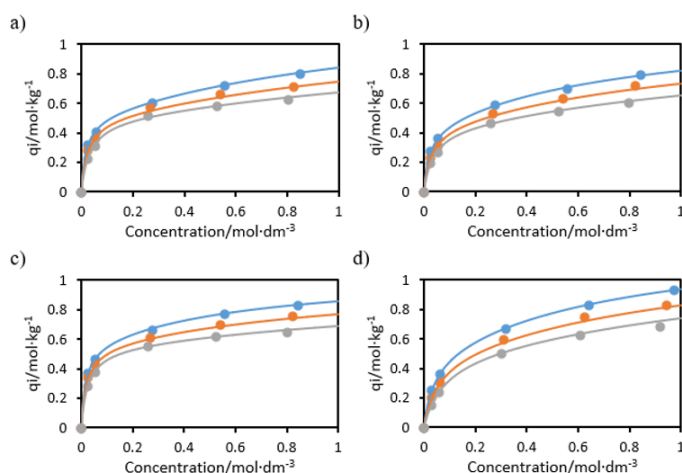


Figure 1. Adsorption Isotherms for: a) *o*-Xylene, b) *m*-Xylene, c) *p*-Xylene, and d) Toluene at 453 K (●), 483 K (●), and 513 K (●). Experimental data (●). Mathematical fit (-).

The higher affinity of *p*-xylene is due to the exchange of Na^+ ions by Ba^{2+} and K^+ which destabilizes the traditional adsorption sites. When these sites are destabilized, they become inaccessible or less energetically favorable to isomers that strongly depend on them, such as *o*-xylene and *m*-xylene, which have bulkier and less symmetric geometries.

However, *p*-xylene being more symmetrical and compact means it does not rely as much on these sites as it can accommodate itself better in alternative sites within the supercage, even with additional steric constraints.

The mathematical model used to fit the experimental data assumes the existence of two distinct types of adsorption sites, which most likely correspond to sites associated with barium and sites associated with potassium.

Table 1. Pseudo single-component Dual-Site Langmuir parameters for *o*-xylene, *m*-xylene, *p*-xylene, and toluene.

	q_{m1} (mol·kg ⁻¹)	$b_{1,0}$ (dm ³ ·mol ⁻¹)	$-\Delta H_1$ (kJ·mol ⁻¹)	q_{m2} (mol·kg ⁻¹)	$b_{2,0}$ (dm ³ ·mol ⁻¹)	$-\Delta H_2$ (kJ·mol ⁻¹)
oX	0.855	0.435	27.7	0.499	40.2	19.1
mX	0.737	0.745	29.5	0.428	36.8	17.4
pX	0.533	0.768	40.6	0.544	50.2	15.8
Tol	0.857	0.767	28.0	0.480	18.3	21.5

The behavior of binary and ternary mixtures was also addressed. In this case, the breakthrough curves for *o*-xylene, *m*-xylene, and toluene showed a roll-up which is a sign of the competition between *p*-xylene and the other components, further supporting the conclusion that *p*-xylene has a higher affinity for the solid phase.

Conclusions

The faujasite zeolite exchanged with barium and potassium shows greater affinity for *p*-xylene than toluene, *o*-xylene and *m*-xylene, which demonstrates it is a suitable absorbent for this separation. These are encouraging results that indicate that this reaction could occur simultaneously with isomerization (such as in a SMBR) as all these components are present.

07. CAPTURA DIRECTA DE CO₂: EL PODER DE LAS ZEOLITAS

Miguel Palomino^{1*}, M. Teresa Navarro¹, Fernando Rey¹, Susana Valencia¹, Tamara Guerrero-Esteban², Micaela Taborga³

¹ Instituto de Tecnología Química (ITQ), Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, 46022-Valencia (España).

² Repsol Technology Lab, C/ Agustín de Betancour s/n, Móstoles, 28935-Madrid (España).

³ Marble Studio, Station F, 5 Parv. Alan Turing, 75013-Paris (Francia)

* miparo@itq.upv.es

En este estudio se ha analizado la influencia de la composición química y topología zeolítica en la capacidad de adsorción de CO₂ de materiales microporosos en condiciones de captura directa del aire (DAC), modificando la relación Si/Al y la naturaleza del catión de compensación de carga en distintas zeolitas. Se ha encontrado que la zeolita chabacita de relación Si/Al=2 intercambiada con Ca es un adsorbente muy prometedor para la captura directa de CO₂ del aire, alcanzando una capacidad de adsorción récord entre los adsorbentes zeolíticos.

Introducción

El calentamiento global, directamente vinculado al aumento de la concentración de CO₂ en la atmósfera, es sin duda uno de los mayores desafíos en la actualidad. Por ello, se han promovido iniciativas de investigación destinadas a la reducción de emisiones de CO₂, así como a su captura en las fuentes de emisión o directamente de la atmósfera y su transformación en productos valiosos. De todos los escenarios de captura de CO₂, la captura directa del aire (DAC) es el más complejo, debido a la bajísima concentración de CO₂ en la atmósfera (aproximadamente 400 ppm). Para adsorber eficientemente el CO₂ del aire en un sólido poroso, el calor de adsorción debe ser relativamente alto, lo que a su vez hace que la regeneración del adsorbente sea energéticamente exigente.

El objetivo de este trabajo es optimizar la capacidad de adsorción de CO₂ de zeolitas en condiciones de baja presión, asegurando al mismo tiempo que el adsorbente siga siendo fácilmente regenerable, es decir, con calores de adsorción moderados. Al inicio de este proyecto, la mayor captura de CO₂ reportada en la literatura era la zeolita X intercambiada con litio (Li-LSX), con una capacidad de adsorción de 1.34 mmol/g a 400 ppm de CO₂ (equivalente a 0,4 mbar de presión absoluta de CO₂) y 25 °C [1]. Más recientemente, se han descrito las zeolitas chabazita (CHA) y mordenita (MOR) intercambiadas con Zn, con capacidades de adsorción en condiciones DAC de 0.67 y 1.15 mmol/g, respectivamente [2,3].

Resultados

Para lograr el objetivo planteado, se realizó un estudio exhaustivo de la influencia de la composición química y topología zeolítica en la capacidad de adsorción de CO₂ de adsorbentes microporosos en condiciones de DAC. Así, se examinó el efecto de la composición química variando las relaciones Si/Al de zeolitas CHA, LTA y FAU. Además, se investigó el papel de los cationes Na, Ca y Zn como compensadores de carga mediante intercambio iónico de las zeolitas. La determinación de las isothermas de adsorción de CO₂ con alta resolución en la zona de ultrabaja presión indicó que la mayor adsorción de CO₂ en condiciones de DAC se logró con zeolitas que contenían Ca y presentaban bajas relaciones Si/Al.

El nivel de intercambio catiónico de Ca varió significativamente entre las distintas zeolitas estudiadas, por lo que se intentó optimizar este parámetro y se encontró que la zeolita Ca-CHA de relación Si/Al = 2 (Ca-CHA-2) presentaba los mejores resultados, especialmente a altos grados de intercambio. Así, se generó una serie de zeolitas Ca-CHA-2 y se analizó su capacidad de adsorción de CO₂ en condiciones de DAC (Figura 1).

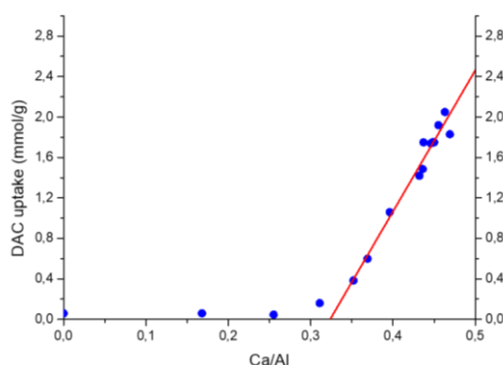


Figura 1. Adsorción de CO₂ en condiciones DAC (0.4 mbar de CO₂ y 25°C) de zeolitas Ca-CHA-2 de distinta relación Ca/Al.

La figura muestra que las zeolitas con relación Ca/Al inferior a 0.35 presentaban baja capacidad de adsorción de CO₂, observándose un aumento casi lineal para relaciones Ca/Al entre 0.35 y 0.5. La mayor adsorción de CO₂ en condiciones DAC se encontró para zeolitas con relación Ca/Al superior a 0.45, es decir, muy cerca del valor máximo teórico de intercambio de 0.5, con capacidades de adsorción superiores a 2 mmol/g [4]. Esta adsorción supera los mejores resultados descritos hasta el momento para zeolitas y corresponde aproximadamente al 40 % de la capacidad total de adsorción de CO₂ de la zeolita.

Un factor clave para la aplicación práctica de la zeolita Ca-CHA-2 es su regenerabilidad. Para evaluarla, se midieron isothermas de adsorción a diferentes temperaturas en condiciones de vacío y temperatura moderadas. Además, la zeolita Ca-CHA-2 optimizada

se sometió a diversos ciclos de adsorción-desorción sin una reducción significativa de su capacidad de adsorción, lo que indica una alta estabilidad. Sin embargo, se requieren evaluaciones adicionales de estabilidad y una investigación detallada de la competencia por el agua durante el proceso de adsorción para evaluar completamente su aplicabilidad práctica.

Conclusiones

La zeolita chabacita de relación Si/Al=2 intercambiada con Ca ha resultado un adsorbente muy prometedor para la captura directa de CO₂ del aire, alcanzando una capacidad de adsorción récord entre los adsorbentes zeolíticos.

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O8. Waste-to-sustainable catalyst strategy: industrial waste as a precursor for highly active H₂S removal materials

Meriem Abid¹, Manuel Martínez-Escandell¹, Rosa Maria Arán-Ais², Elena Albert-Navarro³, Francisca Arán-Ais³, and Joaquin Silvestre-Albero*¹

1 Advanced Materials Lab, Inorganic Chemistry Department, University of Alicante, Spain.

2 Instituto de Electroquímica, Universidad de Alicante, Spain.

3 INESCOP, Footwear Technological Centre, Elda, Spain.

** e-mail of the main author: abidmeriem095@gmail.com*

Hydrogen sulfide (H₂S) is a highly toxic and corrosive pollutant emitted from both natural and industrial sources, requiring efficient removal technologies due to strict environmental regulations. Although various adsorbents such as zeolites, metal oxides, membranes, and activated carbons have been developed, there is growing interest in low-cost, high-performance materials for improved H₂S capture. In this work, chromium-containing activated carbon materials were produced from leather footwear waste and applied for catalytic H₂S decomposition.

Introduction

Hydrogen sulfide (H₂S) is a highly toxic and corrosive air pollutant released from both natural and industrial sources, including anaerobic digestion, geothermal activity, volcanic eruptions, and oil refining [1,2]. Due to its severe environmental and health impacts, strict regulations require efficient technologies for its removal. Over the years, various adsorbent materials such as zeolites, metal oxides, membranes, and activated carbons have been developed for H₂S capture; however, there is still growing demand for low-cost, efficient, and highly reactive materials with improved adsorption and catalytic performance [3]. In this context, waste valorization has emerged as a sustainable approach to develop advanced functional materials. This work focuses on converting chromium-tanned leather footwear waste into activated carbon materials for the catalytic decomposition of H₂S. The synthesized materials exhibit a highly developed porous structure and contain well-dispersed Cr(III) species, which enhance their reactivity. These characteristics enable excellent H₂S removal performance under realistic conditions, highlighting their potential for industrial application. Overall, this study demonstrates an effective strategy for transforming industrial leather waste into value-added catalysts, contributing to both pollution control and circular economy development.

Experimental

Chromium-based catalysts were produced from chromium-tanned leather waste from footwear manufacturing. The leather scraps were first pyrolyzed at 800 °C under

nitrogen to form a carbon material, then ground into a fine powder. This carbon was subsequently activated using CO₂ at 800 °C for 4-6 hours to enhance its properties. The activation conditions were chosen based on thermal analysis showing good reactivity of the carbon at this temperature.

Results

The study demonstrates the successful conversion of chromium-tanned leather footwear waste into highly efficient activated carbon catalysts for H₂S removal. After pyrolysis and CO₂ activation, the materials develop a high surface area (up to ~750 m²/g) and a highly microporous structure. Characterization shows well-dispersed Cr(III)/Cr₂O₃ nanoparticles uniformly distributed on the carbon matrix, which act as active catalytic sites. In breakthrough tests under industrial-like conditions (800 ppm H₂S, 60% humidity, and oxygen), the activated carbons show excellent performance, achieving breakthrough capacities up to ~450 mg/g and operating times exceeding 25 hours. Performance is strongly enhanced by moisture, which promotes surface reactions. Post-reaction analysis confirms sulfur deposition as elemental and oxidized sulfur species, indicating that H₂S is mainly oxidized during the process. The catalysts show good reproducibility and stability, with no significant change in chromium oxidation state after use. **Conclusions** Overall, this work provides the first experimental evidence of converting leather footwear waste into valuable activated carbon-based catalysts. The combination of a highly microporous structure and well-dispersed chromium oxide nanoparticles results in excellent performance for H₂S conversion. These findings highlight a sustainable approach to addressing the environmental issue of leather waste by transforming it into effective catalytic materials.

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O9. UPCYCLING PINE BARK FOR BOSTED TEXTILE WASTEWATER TREATMENT

Ricardo M. Ferreira^{1*}, Olivia S.G.P. Soares¹, Cidália M.S. Botelho¹

¹ LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

* rmmferreira@fe.up.pt

Agro-industrial residues offer a sustainable route for developing low-cost biosorbents for wastewater treatment. In this study, pine bark (*Pinus pinaster*) was transformed into tailored adsorbent materials through high-pressure salt impregnation and subsequent thermal activation. Zinc and calcium chlorides were used as modifying agents, producing biosorbents with distinct surface properties. The performance of the materials was assessed for real textile wastewater decolorization, quantified using Pt–Co colour measurements. Results showed that calcium-modified pine bark consistently outperformed zinc-based materials, particularly after thermal treatment under N₂+CO₂ and N₂+H₂ atmospheres. Colour removal efficiency increased significantly with adsorbent dosage, highlighting the importance of operational conditions in optimizing treatment performance. Under optimized conditions, substantial reductions in effluent colour were achieved, demonstrating effective pollutant removal. Overall, the study confirms that engineered pine bark biosorbents are promising, sustainable, and efficient materials for textile wastewater treatment, with strong potential for scale-up applications in circular water management systems.

Introduction

Textile effluents are typically characterized by intense coloration, high chemical complexity, and the presence of recalcitrant organic compounds, making their treatment particularly challenging for conventional wastewater processes [1]. In this context, lignocellulosic agricultural and forestry residues have gained increasing attention as sustainable and low-cost biosorbents due to their natural abundance, renewability, and surface chemistry rich in functional groups such as hydroxyl, carboxyl, and phenolic moieties, which can promote pollutant binding. Pine bark (*Pinus pinaster*), in particular, represents a promising precursor for engineered adsorbent materials [2]. This work investigates the modification of pine bark through chemical and physical activation strategies to enhance its adsorption performance and evaluate its applicability in the treatment of real textile wastewater systems.

Experimental

Pine bark-derived biosorbents were produced using a high-pressure impregnation process with ZnCl_2 and CaCl_2 solutions, applied at pressures of 75 and 150 MPa for 10 min to promote deeper salt penetration and improved precursor modification. Following impregnation, the materials were subjected to controlled thermal treatments under different atmospheres, namely N_2 , $\text{N}_2 + \text{CO}_2$, and $\text{N}_2 + \text{H}_2$, in order to tailor porosity development, surface chemistry, and structural stability. Batch adsorption experiments were conducted using real textile wastewater to ensure process relevance under practical conditions. Decolorization efficiency was quantified using Pt–Co colour measurements at 400 nm after 24 h of contact time, across different adsorbent dosages (5, 7.5, and 10 g/L), allowing assessment of both material performance and operational parameters.

Results

The type of impregnating salt and the subsequent thermal treatment had a pronounced effect on the adsorption performance of the pine bark-derived biosorbents (Table 1). Materials modified with ZnCl_2 generally exhibited moderated decolorization efficiency, with residual colour values remaining above 95 Pt–Co units, compared to the initial untreated effluent value of 227 Pt–Co. This indicates a limited enhancement of adsorption capacity under the conditions tested. In contrast, CaCl_2 -modified biosorbents demonstrated significantly improved performance, particularly when combined with thermal activation under $\text{N}_2 + \text{CO}_2$ and $\text{N}_2 + \text{H}_2$ atmospheres, which are known to promote pore development and surface reactivity. At a lower adsorbent dosage of 5 g/L, residual colour values ranged between 63 and 79 Pt–Co, reflecting a substantial reduction in effluent colour. Increasing the adsorbent dosage to 7.5 and 10 g/L further enhanced removal efficiency, lowering residual colour to values between 22 and 35 Pt–Co. Overall, impregnation pressure (75 vs 150 MPa) had a comparatively minor influence on performance, while adsorbent dosage and thermal treatment conditions were identified as the dominant factors governing decolorization efficiency.

Table 1. Average real colour (Pt–Co) after 24 h of adsorption treatment, compared to the initial effluent (227 Pt–Co).

CaCl_2	$\text{N}_2 + \text{CO}_2$			$\text{N}_2 + \text{H}_2$		
	5g/L	7.5 g/L	10 g/L	5 g/L	7.5 g/L	10 g/L
75 MPa	67 ± 2	41 ± 1	34 ± 2	80 ± 4	46 ± 3	34 ± 2
150MPa	66 ± 1	37 ± 2	22 ± 2	64 ± 3	35 ± 1	25 ± 2

Conclusions

Calcium-modified pine bark biosorbents prepared via high-pressure impregnation and optimized thermal activation demonstrated high efficiency for textile wastewater decolorization. Adsorbent dosage was identified as a key operational parameter, while impregnation pressure had a minor effect. These findings highlight the potential of pine bark as a sustainable and cost-effective material for wastewater treatment applications.

Acknowledgments

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O10. ADSORCIÓN DE CO₂ POR CAPTURA DIRECTA DE AIRE Y METANACIÓN INTEGRADA CON NANOPARTÍCULAS DE ÓXIDOS MIXTOS DE Ni, Ca y Ce

Arantxa Davó Quiñonero*¹, Santiago García-Pardo Hernández¹, Katia Gómez Villegas¹, José C. Martínez Fuentes¹, Iván Martínez López¹, Dolores Lozano Castelló¹, Agustín Bueno López¹

¹Departamento de Química Inorgánica, Universidad de Alicante, C/ Carretera San Vicente del Raspeig s/n, San Vicente del Raspeig, España (03690)

*arantxa.davo@ua.es

Resumen

Se han preparado nanopartículas mixtas de óxidos Ca-Ni-Ce como materiales duales funcionales (DFMs) para la captura directa de CO₂ del aire y su metanación integrada. Los materiales, sintetizados por doble microemulsión inversa con distintos contenidos de CaO y Ni fijo, presentan tamaños de 4–6 nm y formación de una solución sólida ternaria en la red de ceria. La caracterización confirma una ligera disminución del tamaño de nanopartícula con el aumento de CaO. Los ensayos de TG acoplado a MS muestran buena capacidad de captura de CO₂ y conversión a CH₄. El contenido de CaO ajusta el equilibrio entre adsorción y actividad catalítica, destacando el 9% CaO como el mejor compromiso entre captura y metanación integrada.

Introducción

La captura directa de CO₂ del aire (DAC) sigue siendo uno de los grandes retos actuales debido a la baja concentración de CO₂ en la atmósfera y a la necesidad de procesos energéticamente eficientes.[1] En este contexto, los materiales funcionales duales (DFMs) que integran captura y conversión en un mismo lecho emergen como una estrategia prometedora para simplificar el proceso y mejorar su viabilidad. En este trabajo se preparan nanopartículas mixtas de óxidos Ca-Ni-Ce como DFMs para la captura directa de CO₂ y su metanación integrada, mostrando un comportamiento altamente eficiente.

Experimental

Los materiales se sintetizaron mediante doble microemulsión inversa,[2] incorporando los precursores de Ce, Ni y Ca en una de las microemulsiones. Se prepararon 4 materiales con contenidos de CaO del 0%, 5%, 9% y 22% p., manteniendo constante la carga de Ni en 12% p. Los sólidos se caracterizaron mediante TEM, DRX, adsorción de N₂, desorción

programada de CO₂ y reducción programada con H₂. La capacidad de captura de CO₂ y metanación integrada se evaluaron mediante TG acoplado a espectrometría de masas (MS), monitorizando las señales de CO₂ y CH₄. Tras una reducción previa a 450 °C en H₂/He durante 30 min, la captura de CO₂ se estudió a 300 °C bajo 400 ppm de CO₂/aire. Posteriormente, se introdujo H₂/He y la temperatura se elevó hasta 450 °C (10 °C/min), manteniéndose 30 min. A continuación, se repitió un segundo ciclo de captura e hidrogenación para comprobar la reproducibilidad de las medidas.

Resultados

La caracterización físicoquímica de los materiales frescos muestra la obtención de nanomateriales con tamaños de partícula de 4–6 nm. Las imágenes TEM (Fig. 1a) y las distribuciones de tamaño (Fig. 1b) indican una ligera disminución del tamaño al aumentar el contenido de CaO, lo cual es corroborado por DRX mediante la reducción del tamaño de cristalito de ceria calculado con la ecuación de Scherrer (DS). Los difractogramas de rayos X (Fig. 1c) muestran una segregación moderada de NiO, sin detección de fases ricas en Ca incluso a altas cargas (30% CaO), lo que sugiere la incorporación de Ca²⁺ y Ni²⁺ en la red cúbica de la ceria, formando principalmente una solución sólida ternaria CaxNiyCe1-x-yOδ.

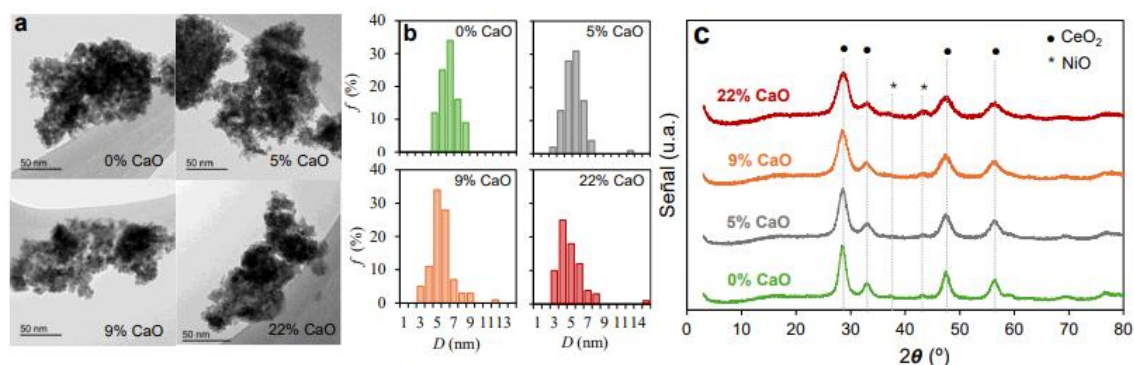


Figura 1. (a) Micrografías TEM; (b) Distribución de tamaños de partícula observados en TEM; (c) DRX de los materiales.

Las isothermas de adsorción de N₂ muestran una clara contracción en las superficies BET calculadas (Tabla 1), con una reducción progresiva desde 96 m² /g para la muestra 0% CaO a 14 m² /g para 22% CaO. Así pues, la inserción de Ca²⁺ reduce, además del tamaño, la microporosidad de las nanopartículas de manera significativa, fenómeno atribuido al proceso de carbonatación y descomposición característicos de la formación del óxido ternario en atmósfera de aire.

Tabla 1. Resultados de caracterización: parámetros de red fluorita (a), tamaño de cristalito Scherrer (D_s) determinados para la ceria a partir de DRX, áreas BET (S_{BET}) a partir de isothermas de adsorción, y capacidad de captura de CO_2 .

Muestra	a (nm)	D_s (nm)	S_{BET} (m^2/g)	mmol CO_2/g ciclo 1	mmol CO_2/g ciclo 2
0% CaO	0.5411	6	96	0.89	0.84
5% CaO	0.5145	5	90	1.05	1.02
9% CaO	0.5111	4	80	1.21	1.18
22% CaO	0.5388	4	14	1.23	1.22

Los resultados de captura de CO_2 (Tabla 1) evidencian una buena capacidad de retención en todos los materiales, estable en dos ciclos de captura y creciente con el contenido de CaO. No obstante, pese a la escasa diferencia en el CO_2 quimisorbido entre las muestras con 9% y 22% de CaO, 9% CaO mostró una producción de metano muy superior durante la hidrogenación, debido a su mayor actividad en metanación.

Conclusiones

La caracterización fisicoquímica confirmó la formación de nanopartículas de óxido mixto Ca-Ni-Ce por el método de microemulsión inversa, con incorporación eficiente de Ca^{2+} y Ni^{2+} en la red de ceria. El CaO mejora la quimisorción de CO_2 , aunque reduce las interacciones Ni-CeOx responsables de la actividad en metanación. El catalizador con 9% de CaO mostró el mejor compromiso entre captura de CO_2 y metanación integrada.

Agradecimientos

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O11. Synthesis of MOF@aluminum saline slag-based composites: A valorization strategy for CO₂ capture at moderate temperatures.

Helir Joseph Muñoz¹, Sophia Korili 1, Antonio Gil^{1*}

¹INAMAT2, Departamento de Ciencias, Universidad Pública de Navarra, Campus de Arrosadía, Pamplona, Spain

* andoni@unavarra.es

Abstract

This research develops innovative MOF@RW1-n* (n = 25, 50, 75) composites by integrating metal-organic frameworks with aluminum saline slag waste (RW1*); these materials were evaluated as CO₂ adsorbents. RW1* acts as a crucial phase-modulator, enabling the selective transition between MIL-96(Al) and MIL-110(Al) structures while improving stability. The resulting hybrid materials exhibit excellent textural properties and thermal stability, promoting a circular economy and reducing the ecological footprint of aluminum production.

Introduction

Rising greenhouse gas emissions necessitate efficient carbon capture technologies [1]. Aluminum-based MOFs (Al-MOFs), particularly MIL-96 and MIL-110, are promising due to their thermal stability and CO₂ capacity, despite complex synthesis requirements [2]. This study proposes using hazardous aluminum saline slag (RW1*) as a cost-effective, eco-friendly modulator for Al-MOF synthesis. By incorporating this industrial byproduct, the research advances a circular economy approach to mitigate the environmental footprint of aluminum production while evaluating its impact on structural and adsorption properties.

Experimental

First, saline slag was treated with 2.0 M HCl (reflux, 100 °C, 2 h) to extract aluminum, yielding residue RW1. RW1 was washed at 80 °C to reduce chlorine content from 16.5% to 0.32% (RW1*). Reference MIL-96(Al) and MOF@RW1-n* (n = 25, 50, 75) composites were synthesized via in-situ hydrothermal method (220 °C, 48 h) using aluminum nitrate and trimesic acid. Products were purified, activated in methanol for five days, and vacuum-dried at 100 °C for characterization.

Results and discussion

X-ray diffraction (XRD) patterns demonstrate that the proportion of RW1* slag significantly affects the predominant crystalline phase (Figure 1 (a1)). Concentrations of 25-50% favor MIL-96(Al), while 75% promotes metastable MIL-110(Al). This structural

shift is corroborated by SEM analysis: the amorphous morphology of the raw slag (Figure 1 (a2)) transitions into well-defined hexagonal prisms at low concentrations (Figure 1 (a3)) and eventually into needle-like structures characteristic of MIL-110 at 75% loading (Figure 1 (a4)). Synthesis boosted BET area from $\sim 32 \text{ m}^2/\text{g}$ (RW1*) to $483 \text{ m}^2/\text{g}$ in the MOF@RW1*-25 composite. The CO₂ adsorption performance was evaluated using a static volumetric method, highlighting the superior efficiency of the synthesized materials relative to industrial benchmarks. At 50 °C, the MIL-96(Al) reference material achieved an adsorption capacity of $1.66 \text{ mmolCO}_2/\text{g}$ (Figure 1b), significantly outperforming several commercial MOFs such as MIL-56(Al) ($1.03 \text{ mmolCO}_2/\text{g}$), Cu-BTC ($1.31 \text{ mmolCO}_2/\text{g}$), Fe-BTC ($0.62 \text{ mmolCO}_2/\text{g}$), UiO-66 ($1.18 \text{ mmolCO}_2/\text{g}$), and ZIF-8 ($0.37 \text{ mmolCO}_2/\text{g}$). The CO₂ adsorption capacities for the MOF composites at 50 and 175 °C are presented in the Figures 1c and 1d. At 50 °C, the maximum capacity ranged from 1.66 mmol/g for pure MIL-96(Al) to 0.12 mmol/g for the saline slag (RW1*), with composites showing intermediate performance. When normalized by surface area, adsorption capacities varied between $2.40 \cdot 10^{-3} \text{ mmol CO}_2/\text{m}^2$ for MIL-96(Al) to $1.95 \cdot 10^{-3} \text{ mmolCO}_2/\text{m}^2$ for the MOF@RW1-75* composite. These results highlight these hybrid materials as high-performance, cost-effective, and sustainable alternatives for carbon capture applications. For more detailed information, please refer to the reference [3].

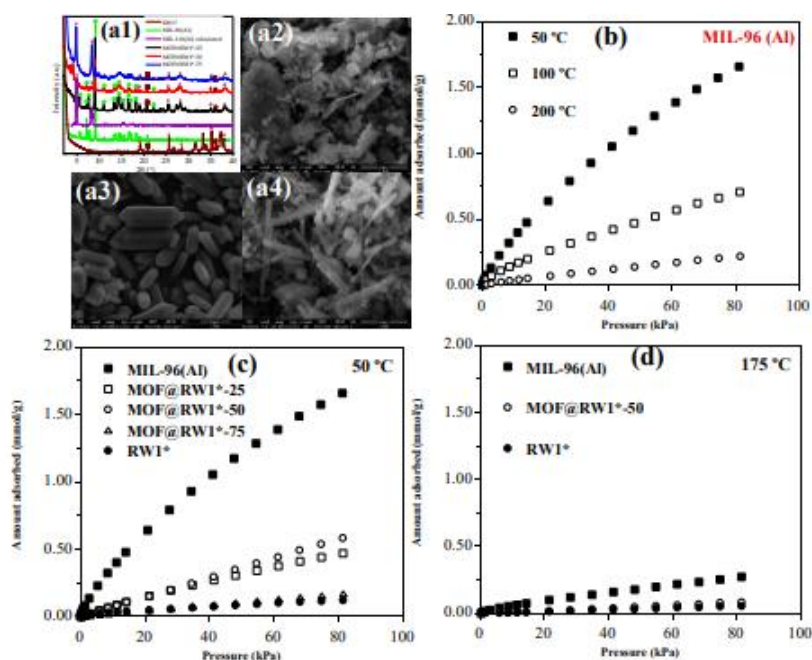


Figure 1. Characterization and CO₂ adsorption performance: (a1) XRD patterns of RW1*, MIL-96(Al), MIL-110(Al) (calculated), and MOF@RW1*-n composites. SEM images of (a2) RW1*, (a3) MIL-96(Al), and (a4) MOF@RW1*-75. (b) CO₂ adsorption capacity for MIL-96(Al) at 50, 100, and 200 °C. Comparative CO₂ adsorption capacity at (c) 50 °C and (d) 175 °C for the materials [3].

Conclusions

MOF@RW1-n* composites were synthesized for the first time via a cost-effective in-situ hydrothermal method using aluminum saline slag (RW1*) as a precursor. XRD and SEM analyses confirmed that a 75% loading of RW1* selectively promotes the formation of the metastable MIL-110(Al) phase, characterized by a distinct needle-like morphology. These findings demonstrate that industrial saline slags are efficient precursors for developing functional MOFs with significant potential for CO₂ capture at moderate temperatures, effectively supporting a circular economy approach.

Acknowledgments

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O12. Selective adsorption behavior in ZIF-90 vs ZIF-8: Modelling and experimental evidence.

Oscar Iván Tovar-Arredondo¹, Carolina Carrillo-Carrión², Ozgur Yazaydin³, Joaquín Silvestre-Albero^{1*}

¹ Department of Inorganic Chemistry–Materials University Institute of Alicante, University of Alicante, Alicante, Spain

² Institute for Chemical Research (IIQ), CSIC–University of Seville, Seville, Spain

³ UCL – London, UK

* joaquin.silvestre@ua.es

Gas separation using porous adsorbents has emerged as an energy-efficient alternative to conventional cryogenic distillation. In this work, ZIF-8 and ZIF-90, two isostructural zeolitic imidazolate frameworks with sodalite topology but different linker functionalities, were comparatively evaluated for light hydrocarbon adsorption and separation. Both materials were synthesized and structurally characterized. Single-component adsorption isotherms of CH₄, C₂H₆, C₂H₄, and C₂H₂ were measured at 25 °C, revealing systematically higher uptakes in ZIF-90, particularly for acetylene. IAST calculations showed that ZIF-90 reverses the selectivity hierarchy observed in ZIF-8, exhibiting enhanced selectivity for the challenging C₂H₂/C₂H₆ separation. Dynamic breakthrough experiments further confirmed the superior separation performance of ZIF-90 under flow conditions. The results demonstrate the critical influence of linker functionality and framework flexibility on adsorption behavior in ZIF materials [1–7].

Introduction

Gas separation processes are among the most energy-intensive operations in the chemical industry, especially for the purification of light hydrocarbons. Adsorption-based technologies employing porous materials have emerged as attractive alternatives to conventional cryogenic distillation due to their lower energy demand and tunable selectivity. Among porous adsorbents, zeolitic imidazolate frameworks (ZIFs) stand out because of their high chemical and thermal stability combined with adsorption-induced structural flexibility [1,2].

ZIF-8 and ZIF-90 are two isostructural MOFs with sodalite topology but different linker functionalities. While ZIF-8 is based on 2-methylimidazolate linkers, ZIF-90 contains imidazole-2-carboxaldehyde linkers, introducing polar aldehyde groups into the pore environment. These differences provide an excellent platform to investigate the role of surface chemistry and framework flexibility on hydrocarbon adsorption and separation performance [3,4].

Experimental

ZIF-8 and ZIF-90 were synthesized following optimized room temperature procedures. The resulting materials were characterized by SEM, XRD, synchrotron XRPD, TGA, and nitrogen physisorption to evaluate their morphology, crystallinity, thermal stability, and textural properties. Single-component adsorption isotherms of methane, ethane, ethylene, and acetylene were measured at 25 °C up to atmospheric pressure, while selectivity values were estimated using IAST calculations. In addition, dynamic breakthrough experiments were performed in fixed-bed columns to evaluate separation performance under flow conditions.

Results

Both ZIFs exhibited high crystallinity and comparable particle sizes, minimizing the influence of particle-size effects during adsorption measurements. In ZIF-8, adsorption followed the trend $\text{CH}_4 < \text{C}_2\text{H}_2 < \text{C}_2\text{H}_4 < \text{C}_2\text{H}_6$, in agreement with previous studies attributing separation behavior to gate-opening effects and diffusion kinetics rather than molecular size [5–7].

In contrast, ZIF-90 showed systematically higher adsorption capacities for all hydrocarbons, with a particularly significant enhancement for acetylene adsorption. IAST calculations revealed that ZIF-90 reverses the selectivity hierarchy observed in ZIF-8, displaying selectivities higher than 1.5 for the challenging $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ separation. This behavior is attributed to the increased polarity of the pore walls and the presence of hydrogen-bond acceptor sites that stabilize acetylene molecules through $\text{C-H}\cdots\text{O}$ interactions and dipole–quadrupole forces [7]. This study was also extended to the challenging $\text{CO}_2/\text{C}_2\text{H}_2$ mixture to further evaluate the influence of framework polarity and flexibility on selective adsorption behavior.

Dynamic breakthrough experiments confirmed the superior separation performance of ZIF-90 under continuous flow conditions.

Conclusions

This study demonstrates that small variations in linker chemistry can produce significant changes in adsorption behavior and selectivity, even in isostructural ZIF materials. The incorporation of polar aldehyde groups in ZIF-90 enhances hydrocarbon-framework interactions and improves separation performance, particularly for acetylene-containing mixtures. These findings highlight the combined importance of surface chemistry and framework flexibility in adsorption-driven separations and provide valuable insights for the rational design of advanced porous adsorbents for energy-efficient hydrocarbon separations [1–7].

Acknowledgments

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O13. Fabrication of UiO-66-NH₂/Fe-Impregnated Activated Carbon Composites for Water Treatment: Synthesis, Characterization and Adsorption Performance.

Sonia Judith Segovia Sandoval^{1*}, Didilia Ileana Mendoza Castillo², Adrián Bonilla Petriciolet², Joaquín Silvestre Albero¹.

¹ *Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Spain.*

² *Tecnológico Nacional de México, Instituto Tecnológico de Aguascalientes, 20256, Aguascalientes, México*

**sonia_segovias@hotmail.com*

Summary

In this work, hybrid adsorbents based on UiO-66-NH₂ and Fe-impregnated activated carbon (FeAC) were developed via two synthesis strategies: in situ MOF growth on FeAC and post-synthetic assembly. The influence of the synthesis route on structural properties and adsorption performance was evaluated. Thorough characterization (BET, XRD, TGA, and XPS) confirmed successful hybridization of UiO-66-NH₂ with the carbon matrix. In terms of performance, all materials showed effective adsorption of both As(V) and fluoride, with higher affinity for As(V). Overall, the hybrid materials demonstrated competitive adsorption performance compared to conventional adsorbents.

Introduction

The presence of As(V) and fluoride in groundwater represents a major environmental and health concern affecting millions of people worldwide. Although WHO guideline limits are 10 µg/L for arsenic and 1.5 mg/L for fluoride [1], these thresholds are frequently exceeded in many regions. Adsorption remains one of the most efficient and scalable water treatment technologies. In this context, metal–organic frameworks (MOFs), particularly UiO-66-NH₂, have emerged as high-performance adsorbents due to their tunable chemistry and exceptional stability. However, their practical implementation is limited by handling difficulties, and recovery constraints. Hybridization with carbon-based materials has emerged as a powerful strategy to overcome these limitations by integrating mechanical stability with adsorption functionality. Herein, we report the design of UiO-66-NH₂/FeAC composites prepared via two synthesis routes and evaluate the impact of synthesis pathway on structure–property relationships and adsorption performance for As(V) and fluoride removal.

Experimental

FeAC was obtained by impregnating RGC-30 activated carbon with 20 wt% Fe, and UiO-66-NH₂ was synthesized following a literature-reported solvothermal procedure [2]. Two 50:50 composites were prepared: UiO-66-NH₂@FeAC by in situ MOF growth on FeAC and UiO-66-NH₂/FeAC by post-synthetic mixing of the preformed materials. Adsorption tests were carried out at pH 7, 30–40 °C, 1 g/L adsorbent dosage, and 10–200 mg/L contaminant concentration, reaching equilibrium after 24 h at 120 rpm.

Results

Nitrogen adsorption–desorption analysis revealed a decrease in surface area upon composite formation, with reductions of 37% (in situ) and 54% (post-synthetic), attributed to pore blockage by Fe species rather than structural degradation, as confirmed by XRD. X-ray diffraction patterns evidenced the preservation of the UiO-66-NH₂ crystalline framework, with characteristic reflections at $2\theta = 7.24^\circ$ and 8.55° , while minor peak shifts in the composites suggest interfacial interactions with the carbon matrix. TGA showed a three-stage decomposition behavior, with main framework degradation at $\sim 390^\circ\text{C}$, consistent with linker decomposition and ZrO₂ formation. XPS confirmed the presence of C, O, N, Zr, and Fe, supporting successful hybrid formation. All materials showed higher affinity for As(V) than fluoride, indicating preferential binding of arsenate species. UiO-66-NH₂ exhibited the highest adsorption capacity for both pollutants. However, UiO-66-NH₂/FeAC (66.7 mg/g) exceeded its theoretical additive capacity by $\sim 42\%$, suggesting a synergistic effect arising from the post-synthetic assembly. This enhancement is likely due to FeAC acting as a support that limits UiO-66-NH₂ aggregation and improves active site accessibility. At pH 7 and 30 °C, UiO-66-NH₂ and UiO-66-NH₂/FeAC achieved 87 and 60 mg/g for As(V), and 35 and 17 mg/g for fluoride, respectively.

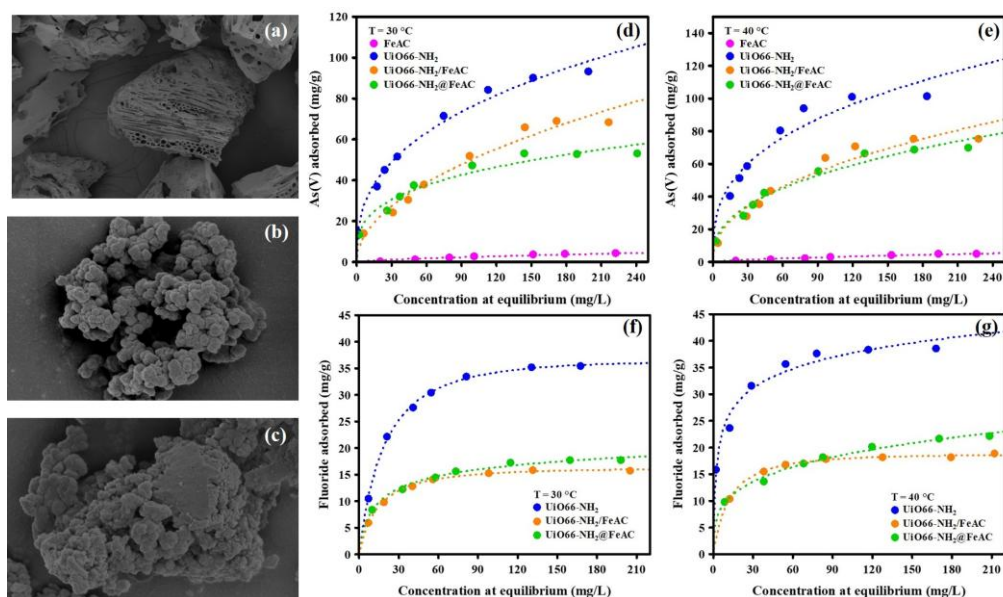


Figure 1. FESEM micrographs of (a) FeAC; (b) UiO-66-NH₂; (c) and (d) UiO-66-NH₂/FeAC. Adsorption isotherms of As(V) (d–e) and fluoride (f–g) on the studied adsorbents at pH 7 and 30–40 °C. Dashed lines indicate the fitted Freundlich (a–b) and Radke–Prausnitz (c–d) models.

Conclusions

This study demonstrates that synthesis pathway critically governs the structural organization and adsorption behavior of UiO-66-NH₂/FeAC composites. Although partial surface area reduction occurs upon hybridization, the resulting materials maintain high adsorption performance while significantly improving structural robustness relative to pristine MOFs. The in situ and post-synthetic strategies yield different interfacial architectures, directly affecting adsorption energetics and performance. These findings highlight the importance of synthesis control in designing MOF–carbon hybrids for multi-contaminant water treatment applications.

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O14. Modulation of adsorbate-framework interactions in ZIF-8 for selective CO₂/CH₄ separation.

M. Karla López González^{1*}, Javier Narciso¹

¹ University Institute of Materials (IUMA), Inorganic Chemistry Department, University of Alicante, Alicante (Spain).

* mariakarla.lopez@ua.es

Summary

Biogas upgrading requires efficient CO₂/CH₄ separation processes combining high selectivity, low energy demand, and stability under realistic operating conditions. In this work, ZIF-8 was post-synthetically modified by incorporating a sulfur-nitrogen ligand to tune the adsorbate-framework interactions governing CO₂/CH₄ separation. The influence of functionalization on the structural, textural, electronic, and adsorption properties was evaluated through complementary characterization, CO₂ and CH₄ adsorption isotherms, and IAST-based separation analyses. The modified materials largely preserved the crystalline structure of the ZIF-8 framework while exhibiting changes in porosity, local electronic environment, and adsorption behavior. Enhanced low-pressure affinity toward CO₂ and improved CO₂/CH₄ selectivity were observed under conditions representative of biogas upgrading. These results highlight post-synthetic functionalization as an effective strategy to tailor MOF adsorbents for selective CO₂/CH₄ separation.

Introduction

The separation of CO₂ from CH₄ is a key step in biogas upgrading processes. Among porous adsorbents, metal organic frameworks (MOFs) have attracted considerable attention because of their tunable pore structure and chemical functionality. ZIF-8 is particularly attractive due to its high surface area, structural flexibility, and relatively high chemical stability under moderate operating conditions. However, pristine ZIF-8 exhibits moderate intrinsic CO₂/CH₄ selectivity, since separation is governed by the interplay between framework flexibility, diffusional restrictions, and limited differential affinity between both gases. In this context, postsynthetic functionalization with heteroatomic ligands containing both nitrogen and sulfur may provide an effective route to selectively enhance CO₂-framework interactions.

Experimental

ZIF-8 was modified through post-synthetic ligand exchange using a S-N ligand at theoretical molar ratios of 1:0.2, 1:0.5, and 1:1, yielding three modified materials denoted as Int.Z2.x-y, where x and y represent the nominal molar fractions of the

original and incorporated ligands, respectively. The materials were characterized by ^1H NMR, PXRD, SEM, N_2 and CO_2 adsorption measurements and XPS. CO_2 and CH_4 adsorption isotherms were collected at 195 and 273 K and fitted using the Sips (Langmuir–Freundlich) model. Binary adsorption equilibria and selectivities were estimated using Ideal Adsorbed Solution Theory (IAST), while PSA working capacities were estimated from equilibrium adsorption isotherms.

Results

^1H NMR confirmed progressive incorporation of the ligand after post-synthetic modification (PSM), increasing with the nominal exchange ratio. PXRD patterns showed that the characteristic sodalite-type crystalline structure of ZIF-8 was preserved for Int.Z2.1-0.2 and Int.Z2.1-0.5, whereas samples with exchange degrees above 66% (Int.Z1.1-1) exhibited partial amorphization. Consistently, SEM images revealed increasing morphological alteration at higher exchange levels while preserving recognizable crystalline domains. XPS analysis of the N 1s region revealed two main nitrogen contributions: one at ~ 398.6 eV assigned to aromatic iminic-type nitrogen species ($\text{C}=\text{N}$) and another at ~ 400.2 eV attributed to electronically depleted and/or noncoordinated nitrogen environments. The increasing contribution of the latter species suggests enhanced electronic heterogeneity after functionalization.

N_2 and CO_2 adsorption measurements showed that PSM modified both the porous structure and adsorption behavior of the materials, leading to the gradual emergence of mesoporosity at higher exchange degrees. Although BET surface area, micropore volume, and total CO_2 uptake at high pressure decreased after functionalization, the modified samples exhibited steeper low-pressure CO_2 adsorption isotherms, indicating enhanced intrinsic affinity toward this gas. These results suggest a progressive shift from a capacity-dominated adsorption regime toward one increasingly governed by stronger adsorbate-framework interactions.

IAST calculations showed that the functionalized materials exhibited progressively higher CO_2/CH_4 selectivities than pristine ZIF-8, particularly at low pressures and low CO_2 molar fractions (Figure 1a-d). This evolution suggests a transition from a separation regime where framework flexibility and microporous confinement play an important role toward one increasingly governed by preferential CO_2 -framework interactions. Notably, the highest selectivities were obtained for the most highly functionalized materials despite their lower surface area and total adsorption capacity, suggesting that selective adsorption becomes increasingly governed by local adsorbate-framework interactions rather than solely by global textural properties. PSA working capacity estimations (Figure 1e) further showed that reversible CH_4 adsorption decreased more markedly after functionalization under competitive conditions, leading to improved

CO₂/CH₄ working capacity ratios, especially for dilute CO₂ mixtures representative of advanced biogas upgrading stages.

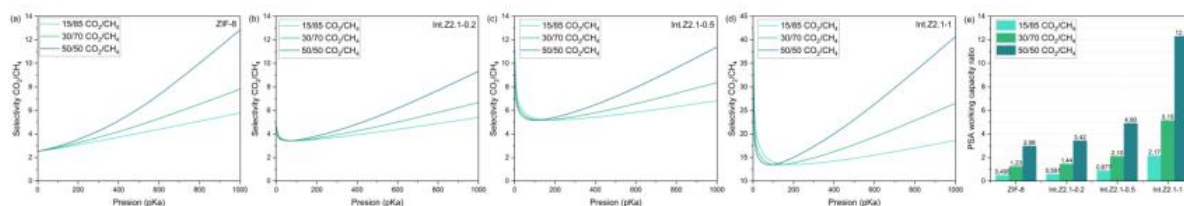


Figure 1- IAST-predicted CO₂/CH₄ selectivities as a function of pressure for (a) ZIF-8, (b) Int.Z2.1-0.2, (c) Int.Z2.1-0.5, and (d) Int.Z2.1-1 under different feed compositions. (e) PSA working capacity ratio for CO₂/CH₄ mixtures.

Conclusions

Post-synthetic modification of ZIF-8 successfully tuned the adsorption behavior of the framework toward enhanced CO₂/CH₄ separation. Increasing functionalization promoted stronger preferential interactions with CO₂ despite reductions in surface area and total adsorption capacity. The modified materials exhibited improved IAST selectivities and PSA working capacity ratios, particularly under low-pressure conditions and dilute CO₂ mixtures relevant to biogas upgrading.

O15. Analysis of ZIF-8 for purification of hydrogen-oxygen mixtures: A molecular simulation study.

I. Sánchez Hernández¹ *; I. Elwakil² ;J. J. Gutiérrez-Sevillano¹

¹Center for Nanotechnology and Advanced Sustainable Technologies (CNATS), Universidad Pablo de Olavide, Avenida Rectora Rosario Valpuesta Fernández 1, 41089, Dos Hermanas, Seville, Spain.

² Department of Chemical Engineering and Chemistry, Materials Simulation & Modeling Group, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, The Netherlands.

* Corresponding author: isanher@upo.es

Hydrogen purification remains an important challenge for hydrogen-based energy technologies, particularly when oxygen impurities are present in gas streams. In this work, the separation of H₂–O₂ mixtures in ZIF-8 was investigated using Grand Canonical Monte Carlo simulations, Molecular Dynamics, and Ideal Adsorbed Solution Theory (IAST). The results showed preferential adsorption of oxygen over hydrogen, especially at low temperatures, due to stronger interactions between O₂ and the ZIF-8 framework. Diffusion analysis indicated that hydrogen diffuses approximately one order of magnitude faster than oxygen inside the porous structure, although separation is mainly governed by adsorption selectivity.

Introduction

Hydrogen purification is a key process for hydrogen-based energy technologies. Among nanoporous materials, zeolitic imidazolate frameworks (ZIFs) are promising because of their high porosity and stability [1]. In particular, ZIF-8 has attracted attention for gas separation due to its sodalite-type porous structure [2]. The crystal structure of ZIF-8 is shown in Figure 1. In this work, H₂–O₂ separation in ZIF-8 was investigated using molecular simulation techniques and IAST calculations in order to evaluate its potential for adsorption-based hydrogen purification.

Methodology

Grand Canonical Monte Carlo simulations were used to calculate adsorption isotherms, heat of adsorption, average occupation profiles, radial distribution functions and energies. Diffusion coefficients were obtained from Molecular Dynamics simulations through analysis of the mean squared displacement. All simulations were performed with the RASPA package [3]. Hydrogen was modeled as a single uncharged Lennard–Jones center following the parametrization proposed by Deeg et al. [4], while oxygen was represented using the three-site model of Harris and Yung [5], which includes both dispersive and electrostatic interactions.

Results and Discussion

The combination of our obtained results showed that oxygen is preferentially adsorbed over hydrogen under all studied conditions. At low temperatures, oxygen adsorption increases significantly because of its stronger interaction with the framework, enhancing selectivity (Figure 2). In addition, hydrogen diffuses faster than oxygen inside ZIF-8 because of its smaller kinetic diameter. However, the separation mechanism is mainly controlled by adsorption selectivity rather than diffusion effects.

Conclusions

ZIF-8 can be a potential oxygen-selective adsorbent capable of enabling indirect hydrogen purification through preferential oxygen removal from the gas phase. The separation performance is favored at low temperatures, where oxygen adsorption is enhanced.

Acknowledgement

This work was supported by the project PID2023-152095NA-I00 “Optimized Membranes for Green Hydrogen Purification”, funded by MICIU/AEI/10.13039/501100011033 and co-funded by the European Regional Development Fund (ERDF/FEDER), European Union.

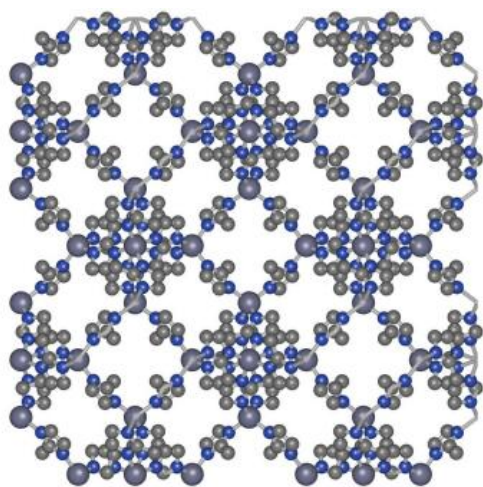


Figure 1. Ball-and-stick representation of the ZIF-8 unit cell showing the sodalite-type framework structure.

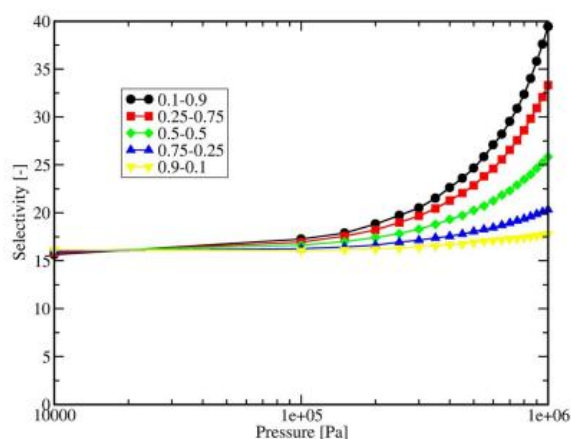


Figure 2. Adsorption selectivity of $\text{H}_2\text{-O}_2$ mixtures in ZIF-8 at 200 K for gas-phase molar fractions of 0.1-0.9 (circles), 0.25-0.75 (squares), 0.5-0.5 (diamonds), 0.75-0.25 (upward triangles), and 0.9-0.1 (downward triangles), corresponding to $\text{H}_2\text{-O}_2$ compositions.

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O16. ADVANCED BIOGAS UPGRADING VIA HYBRID ADSORBENTS IN STRUCTURED DUAL-LAYER ESA PROCESSES.

Luís Madeira^{1*}, Rafael Dias¹, Ana Pereira¹, Ana Mafalda Ribeiro¹, Lasse Wegner², Kalle Mertin², Arne Stölting², Norbert Stock², Alexandre Ferreira¹

¹ LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

² Institute for Inorganic Chemistry, Kiel University, Max-Eyth Straße 2, 24116 Kiel, Germany.

*up202106433@edu.fe.up.pt

Summary

The present work investigates the upgrading of humid biogas via Electric Swing Adsorption (ESA) using a dual-layer monolithic bed. The first layer, composed of CAU-10/Graphite, acts as a pre-drying stage, while the second, CALF-20/AC, performs selective CO₂ capture. Single-component adsorption isotherms of CO₂, CH₄, and N₂ were measured at three temperatures and fitted using appropriate adsorption models. Breakthrough experiments were carried out under dry and humid conditions, each comprising three sequential steps (feed, rinse with pure CO₂, and electrification with N₂ purge). A mathematical model was developed and validated against the experimental data. The results demonstrated preferential CO₂ adsorption and showed that electrification successfully removes adsorbed water, preserving separation performance under humid conditions. The dual-layer ESA concept shows strong potential for humid biogas upgrading, with further work needed on the thermal stability of the CALF-20/AC monolith.

Introduction

The work is framed by the need to decarbonize the energy sector and valorize biogas, composed mainly of CH₄ and CO₂ as biomethane, a renewable substitute for natural gas [1]. Among adsorption-based separation technologies, ESA stands out for enabling fast Joule heating, independent control of the purge flow, and enhanced desorption kinetics, aligning with the European Electrification Action Plan [2]. The central challenge addressed is the presence of water vapor in biogas, which reduces CO₂ selectivity and adsorption capacity [3]. The proposed solution is a dual-layer bed, where the CAU-10/Graphite layer removes water and protects the CALF-20/AC layer responsible for CO₂ capture. The carbonaceous component in each layer provides the conductivity required for Joule heating.

Experimental

Single-component isotherms were determined by the volumetric method at three temperatures (303 K, 323 K, and 343 K). Breakthrough experiments were carried out on the dual-layer bed to represent each of the three sequential steps of the process: feed (60 % CH₄ / 40 % CO₂), rinse with pure CO₂, and electrification with N₂ purge for thermal regeneration of the bed. These experiments were conducted under both dry and humid feed conditions. A mathematical model describing the mass, momentum, and energy balances of the dual-layer bed was developed and solved in *gPROMS* and validated against the experimental data.

Results

CALF-20/AC was well described by the Dual-Site Langmuir model and CAU-10/Graphite by the Single-Site Langmuir model, both showing preferential CO₂ adsorption, as illustrated in Figure 1a) for the isotherms at 303 K. Isostatic heats of adsorption fell within the typical physisorption range, with CO₂ always exhibiting the highest value.

For dry experiments, CO₂/CH₄ separation was demonstrated, with CH₄ breaking through first. The model reproduced all the steps well, with minor limitations. Figure 1b) illustrates the outlet molar flow rate as a function of time for the three sequential steps. As for humid breakthrough, the configuration preserved separation performance in the presence of water vapor, with very low outlet RH during the feed and rinse steps and a pronounced humidity peak (7 % RH) during electrification, confirming effective removal of adsorbed water. The model showed some limitations in describing the water mass-transfer zone.

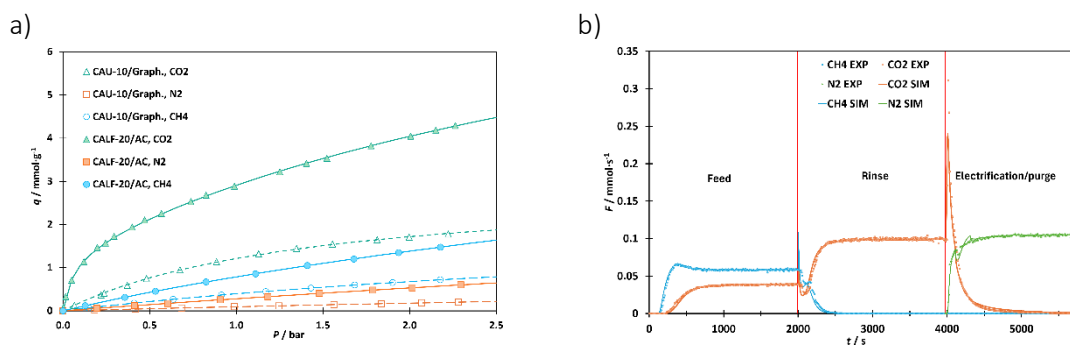


Figure 1 – a) Adsorption isotherms of N₂, CH₄, and CO₂ at 303 K on CALF-20/AC and CAU-10/Graphite (symbols correspond to experimental data and lines to the fitting models);
b) outlet molar flow rate history for the three sequential steps (feed, rinse, and electrification with purge) under dry conditions.

Conclusions

The dual-layer concept demonstrated potential for humid biogas upgrading via ESA: separation is maintained under humid conditions, and electrification effectively

removes adsorbed water. The model represented all three steps well, though with some limitations. The main limitation identified was the thermal stability of the CALF-20/AC monolith, indicating that the composite formulation requires further optimization.

Acknowledgments

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O17. PHOSPHORUS AND POTASSIUM DESORPTION FROM GRASS CLIPPING BIOCHAR AS INFLUENCED BY PYROLYSIS CONDITIONS IN A LAB SCALE DRIP IRRIGATION SYSTEM.

Yesid Murillo-Acevedo¹, Carlos A. Grande^{1,2*}

¹ Laboratory of Intensification of Materials and Processes, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia.

² Chemical Engineering Program, Physical Science and Engineering (PSE) Division, King Abdullah University of Science and Technology.

* carlos.grande@kaust.edu.sa

Biochar derived from grass clippings (St. Augustine, *Stenotaphrum secundatum*) was produced under different pyrolysis conditions to evaluate their influence on physicochemical properties and on the desorption of phosphorus and potassium in a drip irrigation system. The resulting biochars exhibited surface areas ranging from 24 to 187 m²/g and different surface chemistry, with a predominance of basic functional groups. Leachate analysis revealed that P and K are released through different mechanisms, demonstrating the potential of grass-clipping biochar as a nutrient source for soil fertilization. These results contribute to the valorization of urban horticultural waste while offering a sustainable alternative to inorganic fertilizers.

Saudi Arabia has undergone significant urban expansion over the past decade, resulting in a considerable increase in green spaces within urban planning schemes. This growth has led to increased horticultural waste generation, particularly grass clippings, for which the most common disposal methods include landfilling, composting, and mulching. In recent years, biochar has emerged as a sustainable alternative to improve soil fertility and reduce dependence on inorganic fertilizers. Therefore, this study aims to evaluate the effects of pyrolysis conditions on phosphorus and potassium desorption from biochar derived from St. Augustine grass clippings using a laboratory-scale drip irrigation system.

St. Augustine grass clippings were pyrolyzed under a nitrogen atmosphere at 400 °C and 600 °C using slow and fast pyrolysis, producing four biochars: GS400, GS600, GF400, and GF600. These were characterized by TGA, CHNS elemental analysis, BET surface area, WDXRF, and potentiometric titration. Phosphorus and potassium desorption were evaluated by packing 0.2 g of biochar into a laboratory-scale drip irrigation column, using Milli-Q water at 8.3 mL/min, and evaluating leachate fractions by ICP-OES along with pH and electrical conductivity (EC).

The physicochemical properties of the biochars are significantly influenced by pyrolysis conditions, with surface areas ranging from 24 to 187 m²/g and varying surface functional group densities. Notably, biochars produced under isothermal conditions but at different heating rates exhibited distinct surface chemistries, demonstrating that pyrolysis temperature alone is not sufficient to determine biochar properties. These surface chemistry differences play a key role in determining the pH and EC of the leachates, as well as the solubility and transport of P and K ions through the laboratory-scale drip irrigation system. These results highlight that pyrolysis type is a critical parameter that should not be overlooked when preparing biochar for nutrient-release applications.

In conclusion, when producing biochar for nutrient-release applications, pyrolysis temperature alone is not sufficient; the type of pyrolysis must also be considered as a critical parameter. The differences obtained in surface chemistry under different pyrolysis types directly govern the desorption behavior of P and K, reinforcing that biochar properties cannot be predicted from temperature alone. Furthermore, the laboratory-scale drip irrigation system can be considered a reliable methodology to evaluate nutrient release, offering a practical approximation for potential agricultural use.

O18. Sustainable CO₂ Capture Using 3D-Printed Carbon Composites with Fly Ash Integration.

Manon Odelot¹, Inês Correia², Pedro Ouro², Daniel Pereira², Ildefonso Marín-Montesinos², Rui M. Novais³, Luís Mafra², Nuno P. F. Gonçalves², Mirtha A. O. Lourenço^{2*}

¹ Grenoble INP - Phelma, UGA, Graduate School of Engineering in Physics, Electronics, Materials Sciences, France

² University of Aveiro, Chemistry Department, CICECO, Aveiro, Portugal

³ University of Aveiro, DEMaC, CICECO, Aveiro, Portugal

Name of Institution 1 and full address in 11 pt italics.

* mirtha@ua.pt

Abstract

The increasing impact of CO₂ emissions underscores the urgent need for high-performance, sustainable carbon capture materials. Biochar, derived from the controlled pyrolysis of biowaste, has emerged as a promising candidate due to its highly tunable physicochemical properties [1]. This work focuses on the optimization of chitosan-derived biochar adsorbents through tailored synthesis strategies, with particular emphasis on nanostructural evolution governed by polymerization pathways, drying protocols, and pyrolysis conditions [2–4].

A comprehensive set of advanced characterization techniques, including X-ray photoelectron spectroscopy (XPS), in/ex situ solid-state NMR, electron microscopy, and operando TGA-IR, was employed to elucidate the fundamental relationships between synthesis parameters and CO₂ adsorption mechanisms. To move beyond powder-based systems toward scalable, monolithic architectures, N-doped biochars and activated carbons were incorporated into self-standing 3D-printed geopolymer composites, reaching loadings of up to 50 wt.%.

To enable this, a printable ink was formulated comprising the carbonaceous material, metakaolin as the aluminosilicate precursor, fly ash residues, polyethylene glycol (PEG), and an aqueous NaOH solution. Within this formulation, industrial fly ash plays a key synergistic role as a performance-enhancing additive. Our results show that fly ash promotes the formation of interconnected microporous networks, enhances accessible surface area, and significantly accelerates CO₂ adsorption kinetics.

The optimized 3D-printed architectures achieved CO₂ adsorption capacities of up to 1.20 mmol g⁻¹ under continuous flow conditions, while maintaining excellent structural integrity and stable performance over multiple regeneration cycles. Overall, this study

demonstrates a scalable, circular-economy approach to carbon capture by integrating nanostructured carbons, industrial byproducts, and additive manufacturing into functional monolithic adsorbents.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UID/50011/2025 (DOI 10.54499/UID/50011/2025) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020) & UID/PRR/50011/2025 (DOI10.54499/UID/PRR/50011/2025), financed by national funds through the FCT/MCTES (PIDDAC). It has received funding from the European Research Council under the European Union's Horizon Europe research and innovation program (Grant Agreement 865974) and by FCT/MCTES, I.P., through national funds (PIDDAC), co-financed by the European Regional Development Fund (ERDF) of the European Union, through the FEDER program and national funds related to operation no. 16589 (operation code: COMPETE2030-FEDER-00776600) of Portugal 2030 (CharM project). FCT is acknowledged by MAOL for a Junior & Assistant Researcher Positions (CEECIND/01158/2021 & CEECIND/08302/2024). NG and MAOL acknowledge funding from the European Union's Horizon 2020 research and innovation programme No. 101065059 and 101090287, respectively.

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O19. Bridging Structure and Function: Advanced Gas Sorption Characterization of Porous Materials for Storage and Separation.

Nathalia Prieto¹, Riaz Ahmad¹, Christie Baldizar¹, Katie Struckhoff^{1*}

¹ Anton Paar QuantaTec

* Katie.Struckhoff@anton-paar.com

Porous materials continue to attract significant attention for advanced energy technologies due to their high surface areas, tunable porosity, and ability to host or transport energy-relevant species. Their pore structures play a critical role in determining performance in applications such as hydrogen storage, gas separation, capacitive energy storage, and catalytic processes. A detailed understanding of pore size distribution, pore connectivity, and accessible volume is therefore essential for optimizing these materials for next-generation energy systems.

In this study, we investigate meso-macroporous carbons engineered with interconnected pore networks and templated pore diameters of approximately 10 nm, 30 nm, and 150 nm. A combination of characterization techniques—including mercury intrusion porosimetry (MIP), intrusion measurements using a gallium–indium alloy (eGaln), and gas sorption analyses—was employed to evaluate pore structures across a broad dimensional range. Both intrusion methods provided consistent measurements of pore volume and pore size distributions, while density functional theory (DFT) analysis of nitrogen and carbon dioxide gas sorption data yielded complementary insights into the micro- and mesopore regions (Figure 1). BET surface area determinations further supported understanding of accessible surfaces relevant to gas storage processes.

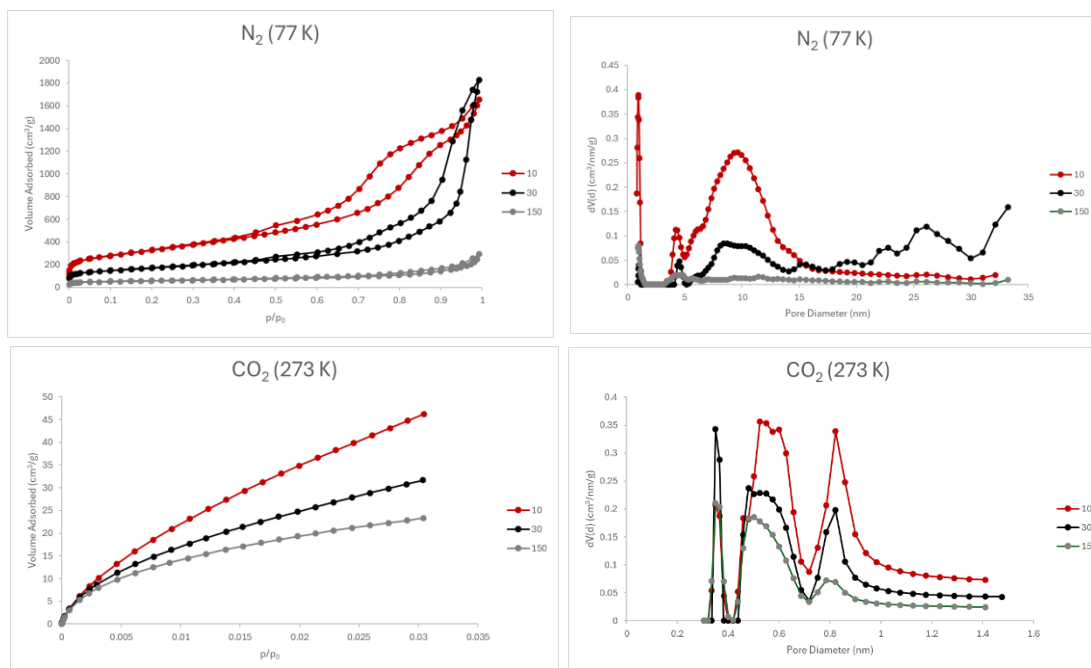


Figure 1-Structural Characterization of hierarchical carbons with gas sorption of N₂@77K and CO₂@273K.

To assess the suitability of these materials for energy storage applications, high-pressure gas adsorption experiments were performed. The mesoporous carbons displayed favorable hydrogen uptake behavior consistent with their tailored pore architectures and high surface areas. The presence of interconnected mesopores was particularly beneficial for facilitating gas transport and improving accessibility under elevated pressures.

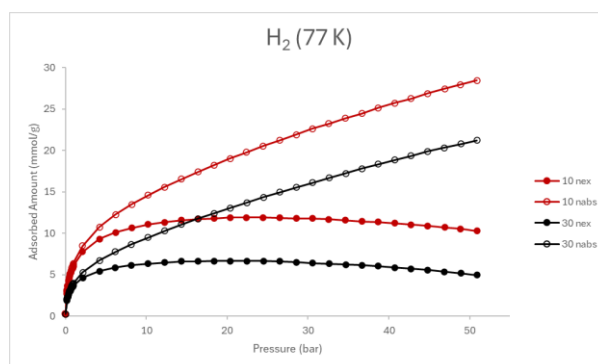


Figure 2- H₂ (77 K) isotherms measured to 50 bar on the 10 and 30 samples

By integrating structural characterization with high-pressure adsorption analysis, this study highlights how tailored pore architectures in mesoporous carbons can enhance performance in hydrogen storage and related energy applications. These findings support ongoing development of engineered carbon materials for emerging clean-energy technologies and demonstrate the value of combining multiple porosity measurement techniques to guide materials design.

O20. Advanced MOF-Based Delivery Systems for Sustained Nitric Oxide Therapy.

Rosana V. Pinto^{1*}, Chen-Chen Cao², Sujing Wang², Guillaume Maurin³, Fernando Antunes⁴, João Pires⁴, Antoine Tissot², Christian Serre² and Moisés L. Pinto²

¹CERENA. Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal.

²Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, 75005 Paris, France.

³Institut Charles Gerhardt Montpellier, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

⁴Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa. Lisboa, Portugal.

* rosana.pinto@tecnico.ulisboa.pt

Summary

This work presents novel Metal-Organic Framework (MOF)-based systems for the controlled delivery of nitric oxide (NO), addressing key limitations of existing carriers such as poor biological stability and short release durations. Three complementary strategies are presented: (i) MIP-177(Ti), a biocompatible titanium-carboxylate MOF enabling 2-hour sustained NO release via a nitrite-forming adsorption mechanism; (ii) MIP-210(Fe), an ultra-microporous iron-bisphosphonate MOF achieving unprecedented NO release exceeding 70 hours in biological media; and (iii) MOF/polycaprolactone (PCL) composite films incorporating MIL-100(Fe) and MIL-127(Fe) that extend release to 8 hours while improving aqueous stability. Preliminary biological results confirm that released NO modulates cellular responses relevant to wound healing, demonstrating the translational potential of these platforms for regenerative medicine and broader therapeutic applications.

Introduction

The therapeutic potential of nitric oxide is well established, yet its clinical use is still constrained by its reactive nature and the lack of delivery systems capable of providing site-specific and sustained release. MOFs featuring open metal sites (OMS) have emerged as promising carriers for NO, enabling high storage via chemisorption and local release of pure NO without toxic by-products [1]. However, key limitations such as poor stability in biological fluids and short NO-release durations (often limited to just a few minutes) have restricted their therapeutic application. To address these limitations and advance MOFs as viable platforms for NO therapy, our research group pursued two

parallel strategies: (i) the rational design of intrinsically stable and biocompatible MOFs with pore environments that promote strong NO coordination; and (ii) the development of MOF/polymer composite systems to fine-tune release kinetics and enable versatile delivery formats.

Results

Using this approach, we identified and engineered new MOFs capable of controlled NO release over distinct timeframes. MIP-177(Ti), a biocompatible and highly stable titanium-carboxylate MOF, enables a 2-hour sustained release via a novel adsorption mechanism involving the formation of nitrites on its framework [2]. In contrast, MIP-210(Fe), an ultra-microporous iron-bisphosphonate MOF, achieves an unprecedented NO-release duration exceeding 70 hours in biological media [3]. This extended-release stems from a unique combination of high chemical stability, ultra-narrow pore architecture, and a distinct adsorption mechanism in which NO preferentially coordinates to Fe(III) centres over water, driven by spatial constraints imposed by free H₂O and P-OH groups within the pores.

As an alternative strategy to enhance the applicability of NO fast-releasing yet promising MOFs, i.e., MIL-100(Fe) and MIL-127(Fe), which are widely used in drug delivery but suffer from limited stability in biological media, we embedded them into hydrophobic PCL matrices to form flexible composite films [4]. This approach significantly extended the NO release duration up to 8 hours and improved the MOFs' chemical stability in aqueous environments. Moreover, the film thickness and MOF loading can be tuned to modulate the NO release rate and duration, allowing adaptation to specific therapeutic applications and delivery routes, including wound dressings, implant coatings, or transdermal patches.

These MOF-based carriers open new possibilities for tailoring NO bioavailability windows, from a few hours to several days, according to the clinical need. Preliminary biological results demonstrated that NO released from both MOFs and composites could modulate key cellular responses involved in wound healing, supporting their applicability in regenerative medicine.

Conclusions

In summary, this work introduces a flexible and effective approach to overcome current limitations in NO delivery using MOF-based and composite platforms. By enabling precise control over release profiles, dosage, and administration formats, these systems represent a promising step toward clinically adaptable NO therapies for a wide range of conditions, including chronic wounds, infections, cancer, and cardiovascular diseases.

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O21. Amino-modified MOFs for the Removal of Nitrates in Contaminated Drinking Water.

Ana Martin-Calvo^{1*}, Tjeu der Kinderen² and Sofia Calero²

¹ Center for Nanoscience and Sustainable Technologies (CNATS). Universidad Pablo de Olavide, 41089, Sevilla, Spain.

² Department of Applied Physics and Science Education Eindhoven University of Technology, 5600MB, Eindhoven, The Netherlands.

* amarc@upo.es

This study evaluates the efficiency of two amino-modified MOFs, MIL-88B-NH₂ and UiO-66-NH₂, for removing nitrates from drinking water using molecular simulations (Monte Carlo methods via RASPA). The simulations revealed that MIL-88B-NH₂ exhibits a significantly superior performance with adsorption of nearly twice as much water and up to 2.9 times more nitrates than UiO-66-NH₂. Due to its enhanced adsorption capacity and robust response to ionic mobility, MIL-88B-NH₂ stands out as a highly promising material for the design of efficient nitrate filtration systems.

Introduction

The presence of nitrates in drinking water sources, largely derived from the use of fertilizers in agricultural practices, represents a continuous source of contamination. To address this issue, metal-organic frameworks (MOFs) emerge as an alternative for water treatment due to their high porosity and large surface area. This work evaluates the nitrate filtration efficiency using two MOFs modified with amino groups: MIL-88B-NH₂ and UiO-66-NH₂. The presence of these functional groups favours the formation of hydrogen bonds, which potentially improves their pollutant adsorption capacity [1,2]. Molecular simulation techniques, specifically Monte Carlo methods using the RASPA software [3], were employed to characterize the materials and model their adsorption capacity, assuming rigid structures. To accurately evaluate nitrate mobility and competitive adsorption, the study divided the simulations into two categories. The first approach modelled nitrate and sodium as independent, freely moving ions (NO₃⁻ and Na⁺) driven by their polarity, which allows them to migrate through the structure to minimize energy. The second approach modelled them as a single, neutral molecule (NaNO₃). From a simulation perspective, the use of this single-molecule model facilitates computational calculations and avoids methodological limitations, proving essential to study and quantify the actual amount of water entering the materials when coexisting with nitrates. Furthermore, different scenarios were explored through simulations with water content fixed at saturation and simulations where both water

and nitrates can freely enter and exit the system, to capture the real behaviour of the adsorption process.

Results

Structural characterization revealed that MIL-88B-NH₂ possesses a significantly larger pore volume (0.8724 cm³/g) and surface area (3063.15 m²/g) compared to UiO-66-NH₂ (0.3734 cm³/g and 904.7 m²/g, respectively). The adsorption simulations further expanded on these structural differences. Water isotherms indicated that while UiO-66-NH₂ slightly outperformed its counterpart at very low pressures, attributed to a higher structural density of amine groups (0.002688 vs. 0.001724 amines/Å³), MIL-88B-NH₂ completely dominated at higher pressures due to its larger available pore space. To probe the true capacity of the materials, total free simulations were conducted where both water and nitrates could freely exchange at realistic environmental pollution concentrations (~20 mg/L). Under these conditions, MIL-88B-NH₂ achieved a nitrate adsorption of 259.47 cm³/g and a water adsorption of 703.17 cm³/g. In contrast, UiO-66-NH₂ only reached 89.88 cm³/g of nitrate and 308.35 cm³/g of water. Furthermore, Average Density Profiles (ADPs) confirmed that structural cavities act as the preferred adsorption sites and that the presence of nitrates did not significantly disrupt the spatial distribution of water.

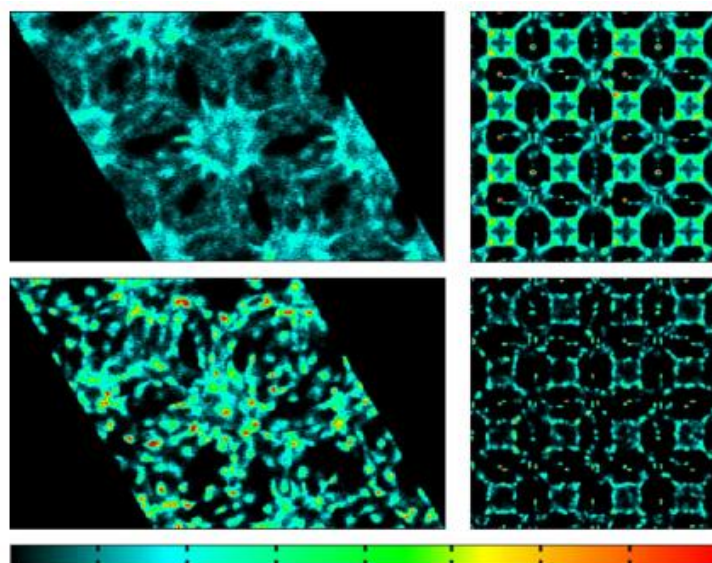


Figure 1. Average density profiles of water (top) and nitrate (bottom) on MIL-88B-NH₂ (left) and UiO-66-NH₂ (right) at 298 K and 100 kPa (XY view).

Conclusions

MIL-88B-NH₂ demonstrates a markedly superior retention performance, being capable of adsorbing up to 2.9 times more nitrates than UiO-66-NH₂. Its excellent structural properties and robust response to ionic mobility position it as a highly promising material for efficient nitrate filtration systems.

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O22. Defect location dictates water adsorption enthalpy in CAU-10-H MOFs.

Diego García-López^{1*}, Giulia van Rossem¹, Norbert Stock², Alexandre F.P. Ferreira³, Sofía Calero^{1*}

¹ *Materials Simulation and Modelling, Department of Applied Physics and Science Education, Eindhoven University of Technology, 5600MB, Eindhoven, the Netherlands.*

² *Institute of Inorganic Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 2, D-24118, Kiel, Germany.*

³ *LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal.*

* *d.garcia.lopez@tue.nl, S.Calero@tue.nl*

Combination of Density-Functional Theory (DFT) calculations and Grand Canonical Monte Carlo (GCMC) simulations were carried out to probe how missing-linker defects in CAU-10-H influence water adsorption thermodynamics and local binding topology. Results showed that, not only defect concentration, but defect position and spatial correlation determine adsorption enthalpy within the framework: isolated defects create high-affinity pockets (stronger adsorption), while adjacent defects tend to reorganize cooperatively, partially mitigating the interaction energy (weaker adsorption). The capacity to tune sorbent affinity through spatial defect control opens a rational pathway to tune water uptake for sorption-based atmospheric water harvesting (SAWH).

Introduction

Water scarcity is one of the most pressing global risks. The situation is becoming increasingly precarious in underdeveloped regions, driving the search for materials that can efficiently harvest atmospheric moisture under arid conditions. Metal-organic frameworks (MOFs), with their tunable porosity and surface chemistry, have emerged as promising sorbents for sorption-based atmospheric water harvesting (SAWH).[1] Among these, CAU-10-H has emerged as a particularly promising candidate for SAWH applications.[2] Furthermore, missing linker defects within the framework structure can modulate water uptake thermodynamics, creating accessible high-affinity pockets for improved atmospheric water harvesting.[3]

Computational Methods

A set of different frameworks containing a range of missing linker motifs were generated. Subsequent geometry optimizations on these frameworks were carried out by means of DFT. Modeling of water adsorption into the CAU-10-H framework was performed using GCMC simulations. The adsorption enthalpy was computed at infinite

dilution (i.e. zero loading) regime as a Boltzmann-weighted average of insertion energies following the Widom insertion method. In this limit, the adsorption enthalpy reflects the framework-adsorbate interactions purely and provides an intrinsic affinity to the MOF. Density-profile distribution plots were also rendered by inserting a single water molecule into the framework pores and allowing its motion across the periodic unit cell through MC moves, providing the spatial probability distribution to reveal the most likely adsorption sites within the framework.

Results

Calculated water adsorption enthalpies span from -25 to -40 $\text{kJ}\cdot\text{mol}^{-1}$, with the most negative values associated with missing linker defects that create accessible, high-affinity pockets (Figure 1, left). Nevertheless, no monotonic trend emerges with defect density alone. Instead, the adsorption energetics reflect the complex correlation between defect topology and local framework relaxation. Spatially separated defects can maintain multiple adsorption pockets and preserve relatively moderate binding, while clustered defects tend to reorganize cooperatively, partially mitigating the interaction energy. Density-profile distributions indicate that high-probability regions are located in the vicinity of the void created by the missing linker, confirming that such defects establish favorable local environments for water adsorption. Overall, despite the linear relationship between water enthalpy of adsorption and defect formation energy (Figure 1, right), missing linker sites with similar electronic energies may exhibit distinct local environments, leading to measurable variability in adsorption enthalpy.

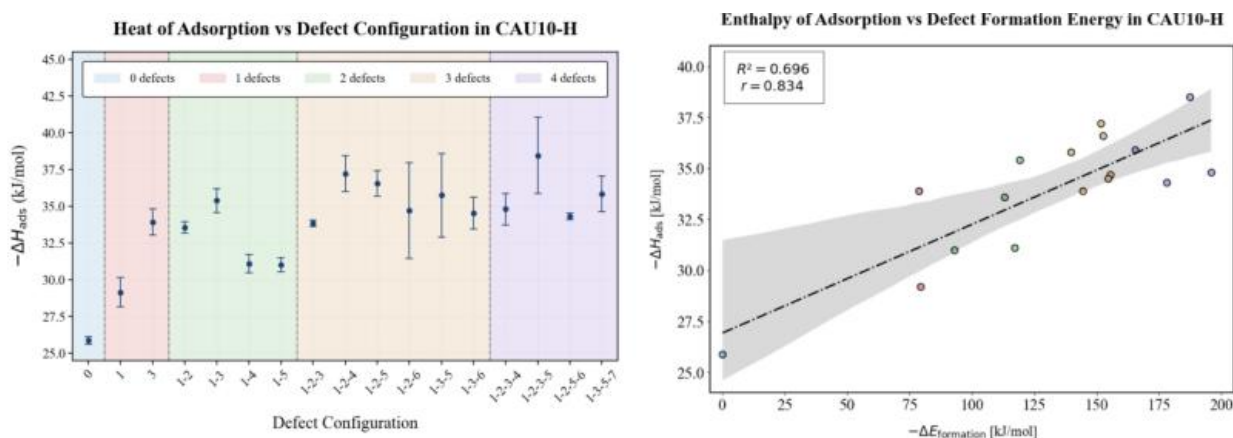


Figure 1. Left: computed heat of adsorption for optimized CAU-10-H and generated defective structures. Right: Enthalpy of adsorption as a function of defect formation energy.

Conclusions

Introduction of missing linker defects enhances water-framework interaction. After structural relaxation, however, the magnitude of the adsorption enthalpy becomes site-specific, spanning a range from 5 to 15 kJ·mol⁻¹ above the pristine structure, depending on the local defect geometry. These findings highlight that, instead of defect concentration, defect topology is the predominant parameter dictating hydrophilicity in CAU10-H. In addition, the established structure–enthalpy relationship offers quantitative guidance for designing MOFs optimized for SAWH.

Acknowledgments

Authors want to thank Water4All/0003/2022 project, a European Partnership under Horizon Europe, for the funding. References [1] *Advanced Functional Materials* 2024, 34, 2304788. [2] *J. Mater. Chem. A* 2016, 4, 11859–11869. [3] *Phys. Chem. Chem. Phys.* 2021, 23, 21329–21337.

O23. MIL-120(Al) towards sustainable biogas upgrading [1].

Marta Bordonhos^{12*}, Rosana Vieira Pinto³, Tânia Frade¹, Bingbing Chen³, Farid Nouar³, Georges Mouchaham³, José R. B. Gomes², Christian Serre³, Moisés Luzia Pinto¹

¹ CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, No. 1, 1049-001 Lisboa, Portugal.

² CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

³ Institut des Matériaux Poreux de Paris (IMAP), ESPCI Paris, École Normale Supérieure de Paris, CNRS, PSL University, 75005 Paris, France

* marta.bordonhos@tecnico.ulisboa.pt

MIL-120(Al), a cost-effective microporous MOF, was tested for CO₂/CH₄ separation. The MOF was produced at the kilogram scale via green-synthesis conditions and shaped into spherical beads without significant loss in adsorption performance. MIL-120(Al) shows a good adsorption capacity for CO₂, higher than that for CH₄. GCMC molecular simulation studies revealed a probable rotation of the μ -OH groups with increasing CO₂ pressure, altering the CO₂ adsorption capacity at higher pressures. Breakthrough experiments confirmed the CO₂/CH₄ selectivity of MIL-120(Al) and showed that the material can retain its original adsorption separation performance after regeneration, following consecutive cycles and prolonged exposure to high amounts of water vapour, demonstrating the potential of this MOF for biogas upgrading.

Introduction

The demand for sustainable energy sources has been growing over the years, driving intensified research into biogas upgrading, a critical process to increase CH₄ purity in raw biogas by removing excess CO₂. Raw biogas can contain up to 50 % (V/V) in CO₂, along with moisture and other contaminants, that limit its direct use as a replacement to fossil natural gas. Adsorption-based cyclic processes like pressure swing adsorption (PSA) can be used for the efficient removal of CO₂ to obtain biogas with a high CH₄ molar content (> 96 %), comparable to conventional natural gas[2,3]. Metal-organic frameworks (MOFs) are versatile hybrid porous materials that have emerged as promising candidates for this application [3]. MIL-120(Al) is an aluminium-based MOF with a great potential for biogas upgrading by adsorption processes due to its high stability toward coordinating and corrosive gases, its cost-effectiveness, and green and scalable synthesis protocol [4].

Results and Discussion

For the complete experimental and simulation details please refer to Bordonhos et al. [1]. MIL-120(Al) was successfully synthesised at the kilogram scale following an environmentally friendly, scalable and high-yield synthesis method, and shaped into beads without significant loss of adsorption performance (not shown here, cf. Ref. [1]). The MOF shows a much higher adsorption capacity for CO₂ than for CH₄ (Figure 1A). GCMC simulations show different CO₂ isotherms, with structures Str1 and Str2 [4] being closer to the experimental isotherm at lower and higher pressures, respectively. This suggests a possible rotation of the μ 2-OH groups in MIL-120(Al), that shifts the MOF

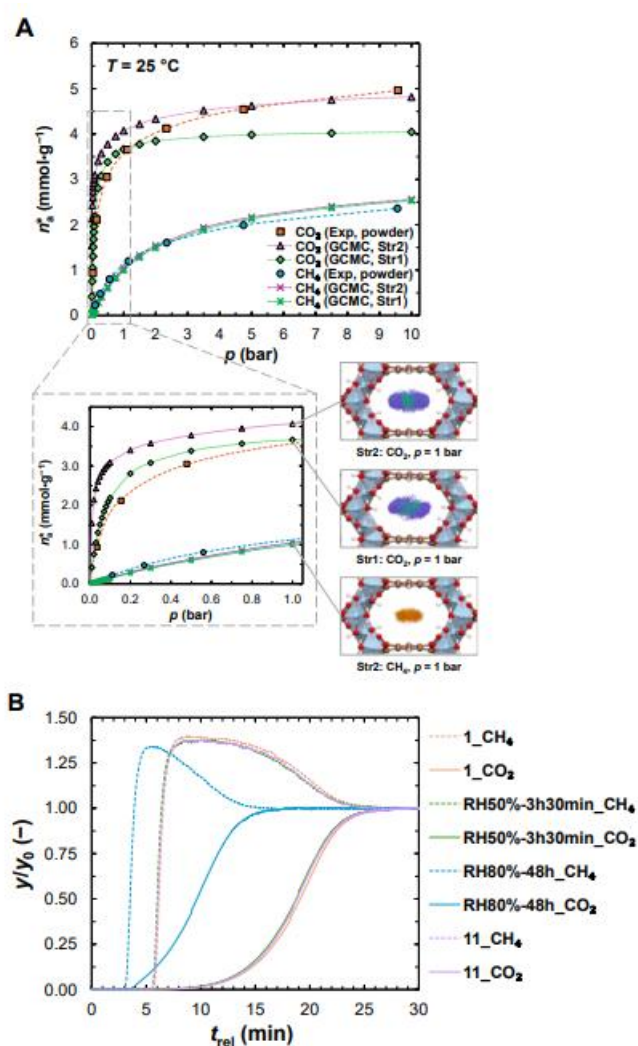


Figure 1. A) Pure CO₂ and CH₄ experimental isotherms at 25 °C for MIL-120(Al) (powder) and calculated by GCMC for Str2 and Str1, and density plots generated from GCMC simulations at 1 bar for CO₂ in Str2 and Str1 and CH₄ in Str2; B) Overlap of the adsorption branch of the CO₂ and CH₄ equimolar mixture breakthrough curves of runs 1, RH50%-3h30min, RH80%-48h, and 11, measured at 25 °C and ca. 1 bar for the shaped MIL-120(Al). Adapted from [1].

between the two configurations as CO₂ pressure increases. The performance of MIL-120(Al) is comparable to other adsorbents, outperforming activated carbons and carbon molecular sieves, and presenting a mixed behaviour in comparison to other MOFs and zeolites [1].

Breakthrough (BT) experiments performed on the shaped MIL-120(Al) for an equimolar CO₂/CH₄ mixture (run 1, orange lines in Figure 1B) confirmed that the MOF is more selective toward CO₂. MIL-120(Al) is also able to retain its separation performance after consecutive BT cycles following regeneration under helium flow, only showing a reduction in CO₂ capacity from the first to the second cycles (not shown here, cf. Ref. [1]). The performance of MIL-120(Al) with trace amounts of water vapour pre-adsorbed was similar to under dry conditions (not shown here, cf. Ref. [1]). BT experiments run after exposing the MOF beads to water vapour with a relative humidity (RH) of 50 % for

ca. 3 h 30 min led to no meaningful losses in the separation performance (green lines in Figure 1B). Only when the material was exposed for 48 h to water vapour at RH = 80 %, was a significant loss of the CO₂/CH₄ separation performance observed (blue lines in Figure 1B). However, after full regeneration (overnight vacuum, followed by activation at 150 °C under helium flow for 12 h), MIL-120(Al) regained its separation capacity (run 11, pink lines in Figure 1B). This performance is in clear contrast with hydrophilic zeolites (with low Si/Al ratios), that can be severely affected by water [5].

Conclusion

MIL-120(Al) was synthesised, shaped and tested for CO₂/CH₄ separation. The MOF shows a good performance, in line with other adsorbents. GCMC simulations suggest a possible rotation of metal cluster μ_2 -OH groups with increasing CO₂ pressure. BT experiments confirmed the selectivity of MIL-120(Al) for CO₂. MIL-120(Al) maintains its performance after consecutive BT cycles and pre-exposure to water vapour, losing capacity only after prolonged exposure to high RH, that is fully reverted after regeneration. MIL-120(Al) can thus be seen as a viable candidate for biogas upgrading by adsorption-based processes.

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O24. FROM POWDER TO STRUCTURED ADSORBENT: 3D-PRINTED ZIF-8 MONOLITHS FOR C₂H₆/C₂H₄ SEPARATION.

Gerson Rincon^{1,2}, Julio E. Sosa³, Henry Ortega-Ortiz^{1,4}, Jeniffer Carrillo⁵, Debora A. Nabarlatz², Laura M. Esteves⁶, Luisa Neves¹, José P.B. Mota¹, Rui P.P.L. Ribeiro^{1,*}

¹ LAQV-REQUIMTE, NOVA School of Science and Technology, NOVA University of Lisbon, Portugal

² Research Group on Technologies for the Valorization of Waste and Agricultural and Industrial Sources for Energy Sustainability (INTERFASE), Universidad Industrial de Santander, Colombia

³ Center for Process and Environment Engineering (CEPIMA), Universitat Politècnica de Catalunya, Spain

⁴ HyLab - Green Hydrogen Collaborative Laboratory, Portugal

⁵ Chemical Engineering Group, Engineering and Architecture Faculty, Universidad de Pamplona, Colombia

⁶ Centro de Química Estrutural (CQE), Instituto Superior Técnico (IST), Universidade de Lisboa, Portugal

* rpp.ribeiro@fct.unl.pt

Ethane/ethylene separation is a critical and energy-intensive process in the petrochemical industry, mainly because of the close physicochemical properties of both molecules. Adsorption-based technologies represent a promising alternative to conventional cryogenic distillation, particularly if ethane-selective adsorbents are available. In this work, structured ZIF-8 monoliths were fabricated by Direct Ink Writing (DIW) using bentonite as a binder to guarantee printability and mechanical integrity. The printed monoliths were characterized in terms of textural, morphological, and thermal properties. Single component adsorption equilibria of ethane and ethylene were measured at 283, 303, and 323 K and compared with pristine ZIF-8. The results indicate that 3D printing is a suitable strategy to structure ZIF-8 while preserving relevant adsorption properties for C₂H₆/C₂H₄ separation.

Introduction

Ethylene is a key platform chemical in the petrochemical industry, particularly as a precursor for polymer production. It is mainly obtained by steam cracking, where ethane and ethylene are produced within complex hydrocarbon mixtures. Due to the similar molecular size, boiling point, and physicochemical properties of C₂H₆ and C₂H₄, purifying ethylene to polymer-grade purity, typically above 99.95%, requires highly demanding separation steps [1]. Although effective, conventional cryogenic distillation involves high energy consumption and substantial operating costs.

Adsorption-based processes, such as pressure swing adsorption, have been proposed as more energy-efficient alternatives. Ethane-selective adsorbents are especially attractive

because they enable ethylene recovery as the less strongly adsorbed component during the feed step, promoting more efficient processes [2]. Metal–organic frameworks (MOFs) are promising candidates for this application due to their tunable pore structures, high surface areas, and adjustable chemical functionality [1,2].

Among MOFs, ZIF-8 is particularly relevant because of its high thermal stability, hydrophobic character, microporous structure, and reported preferential adsorption of ethane over ethylene [3]. However, ZIF-8 is typically synthesized as a fine crystalline powder, limiting its direct use in fixed-bed adsorption processes due to pressure drop, handling, attrition, and scale-up issues. Therefore, shaping MOFs into mechanically stable macroscopic structures is essential to translate their intrinsic adsorption performance into practical separation applications.

Experimental

ZIF-8 monoliths were fabricated by Direct Ink Writing (DIW) using printable inks composed of ZIF-8 and bentonite as binder. The selected formulation contained 15 wt.% bentonite. After printing and drying, the resulting monoliths were characterized in terms of textural properties, morphology, and thermal stability. The adsorption performance of the printed ZIF-8 monoliths was evaluated by measuring single-component equilibrium isotherms of ethane and ethylene at 283, 303, and 323 K. The experimental isotherms were fitted using the Toth model. The ideal adsorbed solution theory (IAST) was employed to predict the multicomponent (C_2H_6/C_2H_4) adsorption and calculate selectivity. The performance of the structured material was compared with pristine ZIF-8 to assess the effect of the 3D-printing process on the material properties.

Results and conclusions

The DIW approach enabled the preparation of self-standing ZIF-8 monoliths. The incorporation of bentonite allowed the formulation of printable inks and ensured the structural stability of the printed bodies. Textural characterization showed that the monolith retained a large fraction of the microporosity of pristine ZIF-8, with an approximate 16% reduction in specific surface area. The material preserved relevant adsorption properties, while SEM-EDS analysis confirmed adequate binder integration and TGA demonstrated that the characteristic thermal stability of ZIF-8 was maintained. Although a slight decrease in adsorption capacity was observed compared with pristine ZIF-8, ethane and ethylene adsorption isotherms confirmed that the structured ZIF-8 monolith retained preferential adsorption toward ethane over ethylene. The Toth model adequately described the equilibrium data, and IAST calculations indicated C_2H_6/C_2H_4 selectivity values higher than 1.74. Overall, these results demonstrate that 3D printing is a promising strategy to transform ZIF-8 powders into structured adsorbents while preserving their potential for energy-efficient ethane/ethylene separation.

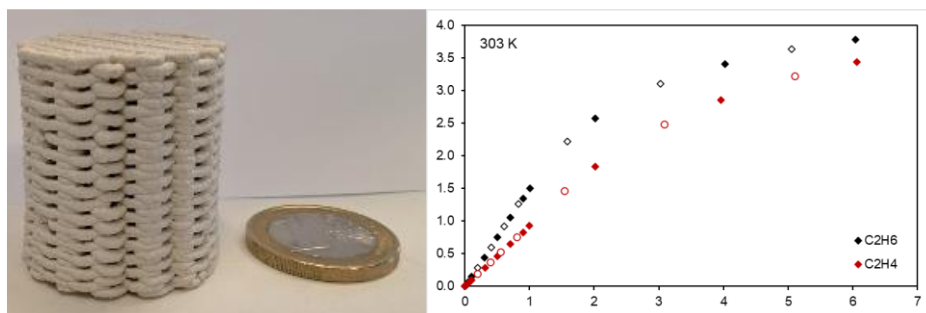


Figure 1. ZIF-8 monolith printed by DIW (left). C_2H_6 and C_2H_4 adsorption equilibrium isotherms at 303 K (right).

Acknowledgments

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O25. TAMOF-1 for CO₂ capture from flue gas.

Susanne Gooijer¹, Santiago Capélo², Esteban Acuna-Yeomans¹, Stefano Giancola³, David Dubbeldam⁴, José-Rámon Galán Mascaros², José-Manuel Vicent Luna¹, Sofía Calero^{1*}

¹ *Materials Simulation and Modelling, Department of Applied Physics and Science Education, Eindhoven University of Technology, PO Box 513, 5600MB Eindhoven, The Netherlands.*

² *Institute of Chemical Research of Catalonia (ICIQ-CERCA), the Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, Tarragona 43007, Spain.*

³ *Orchestra Scientific SL, Av. Països Catalans 16, Tarragona, 43007, Spain.*

⁴ *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands.*

** s.calero@tue.nl*

This work evaluates the potential of the metal–organic framework TAMOF-1 for CO₂ capture from flue gas using a combined experimental and multiscale simulation approach. Grand canonical Monte Carlo simulations accurately reproduce experimental adsorption isotherms of CO₂ and N₂, revealing a stepwise CO₂ adsorption mechanism driven by favorable van der Waals and electrostatic interactions near Cu²⁺ sites. Simulation based predictions of the separation performance and fixed-bed breakthrough behavior demonstrate high CO₂/N₂ selectivity, also in the presence of other flue gas components (NO_x and O₂). Pelletization retains the overall adsorption capacity by ~75% and preserves the separation performance. The sensitivity to water was also predicted in mixtures and until 100 ppm H₂O present in the mixture the CO₂-uptake was not affected. Overall, TAMOF-1 exhibits strong adsorption capacity, selectivity, and stability, highlighting its promise as a robust material for CO₂ capture under realistic conditions.

Introduction

Adsorption in Metal Organic Frameworks (MOFs) can be an energy-efficient method for CO₂ capture from flue gas. The triazole acid MOF TAMOF-1 is constructed from histidine-derived linkers and Cu²⁺ nodes.[1,2] These precursors are inexpensive, do not contain critical raw materials, and enable a straightforward synthesis. To assess the adsorption and separation performance of TAMOF-1, atomistic simulations based on a theoretical model provide many benefits for screening MOFs, as experiments can be costly and time-consuming. The goal of this work is to comprehensively assess the adsorption, separation, and stability performance of TAMOF-1 for CO₂ capture from flue gas under realistic conditions using combined experimental and multiscale simulation approaches.

Methodology

We calculated adsorption isotherms and heats of adsorption by performing grand canonical Monte Carlo simulations using the RASPA software package. The separation of multi-component gas mixtures, both in equilibrium and fixed-bed breakthrough predictions, was modelled using a numerical method based on the ideal adsorption solution theory (IAST) implemented in the RUPTURA software. The simulations were validated by experimental adsorption isotherms and fixed-bed breakthrough experiments.

Results and Discussion

GCMC simulations accurately reproduce experimental adsorption isotherms of CO₂ and N₂. They reveal a step-wise adsorption mechanism for CO₂ with preferential adsorption sites located in highly confined pore spaces near multiple Cu²⁺ centers. The combination of favorable van der Waals and electrostatic interactions of these sites results in high CO₂/N₂ selectivities. Calculated adsorption isotherms and energy decomposition analysis of other compounds present in flue gas (SO₂, NO₂, NO, N₂O, and O₂) showed that adsorbates that cannot exploit both types of interactions, such as NO₂ and NO, exhibit weaker adsorption strengths. These results were confirmed by combined breakthrough simulations and experiments, that revealed efficient separation of CO₂ from a mimicked flue gas mixture containing small concentrations of NO_x compounds.

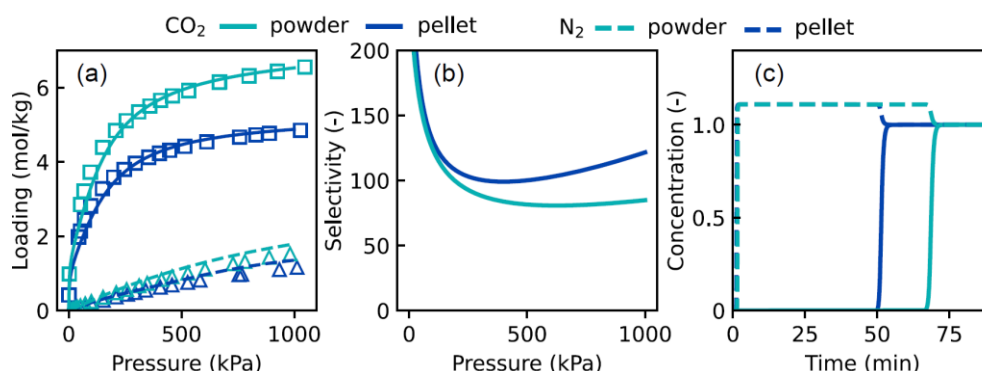


Figure 2: Comparison of the adsorption and separation performance of powdered and pelletized TAMOF-1 crystals. (a) Experimental (symbols) and simulated (lines) pure component isotherms of CO₂ and N₂. (b) Predicted selectivities of CO₂ of the adsorption of a 10:90 CO₂:N₂ mixture. (c) Simulated breakthrough curves for the same mixture.

An important factor for upscaling the separation device is the pelletization of the powder into larger particles. The adsorption isotherms reveal that pelletization reduces the adsorbate capacity by approximately 25% across the entire pressure range studied, consistent with the expected dilution imposed by the inert binder content (20 ~wt%) (Figure 1). Numerical simulations predicting IAST selectivities and breakthrough curves show that the CO₂/N₂ separation performance remains effectively unchanged, with high

selectivities and retention of CO₂ over N₂. Finally, we investigated the interaction between H₂O and TAMOF-1 using a machine learned interatomic potential. We also measured and simulated H₂O isotherms, which combined with IAST calculations, indicated that until 100 ppm of H₂O present in the mixture the CO₂-uptake was not affected.

Conclusions

Overall, this combined experimental-computational study demonstrates the robustness of TAMOF-1 in realistic multicomponent environments and highlights its strong potential for CO₂ capture applications.

Acknowledgments

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O26. Molecular Simulation for Hydrogen Production: Zeolite Confinement Shifts Equilibrium in Steam-Methane Reforming.

J.J. Gutiérrez-Sevillano^{*1}, B. Zhakishева², P.J. Merklings¹, S. Calero²

¹ Center for Nanoscience and Sustainable Technologies (CNATS), Universidad Pablo de Olavide, Avda. Rectora Rosario Valpuesta 1, 41089 Dos Hermanas, Seville, Spain.

² Department of Chemical Engineering and Chemistry, Materials Simulation & Modeling Group, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, The Netherlands.

* jjgutierrez@upo.es

Steam methane reforming (SMR) remains the dominant industrial route for hydrogen production, yet its highly endothermic nature demands elevated temperatures, resulting in substantial energy input and CO₂ emissions. In this work, we investigate whether thermodynamic confinement within nanoporous materials can alter the confined-phase composition under SMR-relevant conditions and evaluate the potential equilibrium shift in coupled reaction-separation systems towards enhanced hydrogen production at lower temperatures.

Methodology

Molecular simulations were performed to quantify confinement induced changes in composition under realistic process conditions. The steam methane reforming reaction was simulated in the bulk using a combination of the Monte Carlo method in reaction ensemble (RxMC) with the continuous fractional component Monte Carlo technique (CFCMC)[1] using the RASPA code[2]. We validate our molecular models against experimental bulk-phase data, and then systematically compare confinement-induced composition changes in large- and small-pore zeolites. Results and Discussion Our results reveal that large-pore zeolite FAU, in both hydrophilic (NaX) and hydrophobic (pure silica) forms, fails to outperform the bulk. In contrast, the small-pore zeolite ITQ-12 shows hydrogen enrichment in the confined phase (see figure 1). At 1 bar and 675 °C, ITQ-12 achieves hydrogen mole fractions comparable to those in the bulk at 825 °C, representing an apparent 150 °C reduction in temperature with potential for considerable energy savings. Zeolite RHO, despite similar pore size, shows no such improvement, highlighting the critical role of channel geometry and topological confinement. These findings demonstrate that properly selected zeolite topologies can thermodynamically steer SMR towards more sustainable conditions [3].

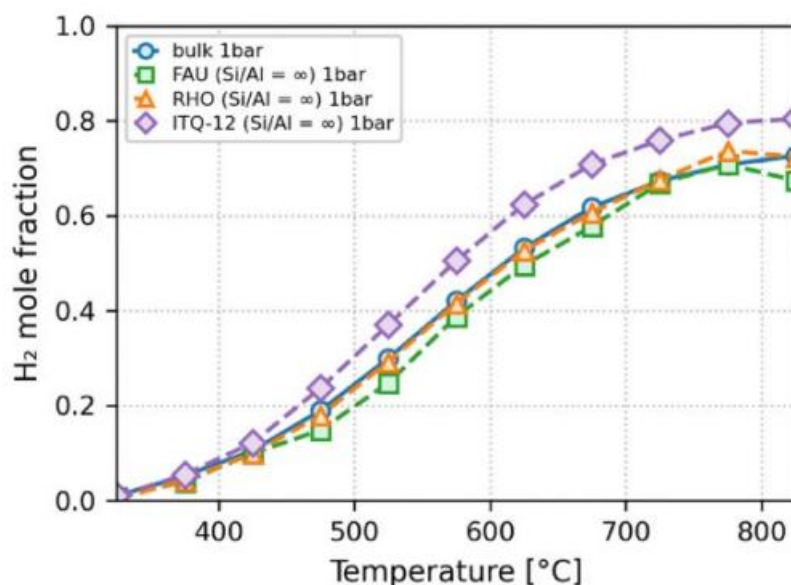


Figure 1. Mole fractions of H₂ at equilibrium within zeolites FAU, RHO, ITQ-12 and in the bulk at 1 bar.

Acknowledgements

This study was funded by the Spanish Ministerio de Ciencia e Innovación (IJC2018-038162-I). We thank C3UPO for the HPC support.

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O27. Geopolymer–Zeolite 13X Composite Adsorbents: From Powder to Structured Architectures for CO₂ Capture.

Mariana Schneider^{1,2}, Mar Calzado-Delgado³, Enrique Rodríguez-Castellón², M. Olga Guerrero-Pérez³, Dachamir Hotza¹, Agenor DeNoni Junior¹, Regina Fátima Moreira¹

¹ *Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Florianopolis, Brazil*

² *Departamento de Química Inorgánica, Instituto Interuniversitario de Investigación en Biorrefinerías I3B, Universidad de Málaga, Málaga, España.*

³ *Departamento de Ingeniería Química, Escuela de Ingeniería Industrial, Universidad de Málaga, Málaga, España.*

The increasing atmospheric concentration of CO₂ requires the development of efficient capture and utilization strategies. Among available technologies, adsorption using solid materials has gained attention due to its lower energy demand and operational flexibility compared to conventional absorption processes. In this work, geopolymer/zeolite 13X composites were developed as functional adsorbents for CO₂ capture. These materials combine the low-cost and sustainable nature of geopolymers with the high adsorption capacity and selectivity of zeolites. Different material configurations were explored, including powder adsorbents, electrospun fibrous membranes, and 3D-printed structured architectures. The results demonstrate that the incorporation of zeolite enhances surface area and adsorption capacity, while structuring the material significantly improves mass transfer, reduces pressure drop, and facilitates regeneration. Overall, this study highlights the potential of geopolymer-based composites as versatile and scalable adsorbents for CO₂ capture, contributing to process intensification and sustainable carbon management.

Introduction

Among CO₂ separation technologies, adsorption stands out due to its relatively low energy requirements, fast regeneration (e.g., PSA and TSA processes), and the possibility of tailoring solid materials to optimize performance. However, conventional adsorbents, typically in powder or pellet form, suffer from limitations such as diffusion constraints, high pressure drop, and poor mechanical stability during cycling. To overcome these limitations, the development of functional structured materials is essential. In this context, geopolymers are promising due to their low-cost synthesis from aluminosilicate sources, high thermal and chemical stability, and potential incorporation of industrial waste streams. On the other hand, zeolite 13X is a well-established adsorbent characterized by high surface area, microporosity, and strong affinity for CO₂. This work focuses on the design of geopolymer/zeolite composites and their structuration into

advanced configurations such as electrospun fibers [1] and 3D-printed architectures to enhance CO₂ adsorption performance and process efficiency.

Results & Discussion

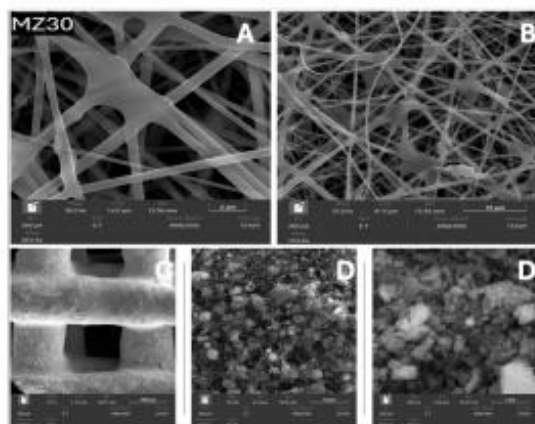


Figure 1. SEM images of (A,B) electrospun fibers (geopolymer/zeolite30%/PVA) and (C,D,E) 3D printed geopolymer/zeolite 13X composites sample.

The results show that geopolymer/zeolite 13X composites were successfully synthesized, combining the amorphous geopolymer matrix with the crystalline structure of zeolite, which preserves its adsorption properties and leads to materials with competitive CO₂ uptake, where the adsorption capacity increases with zeolite content due to the associated rise in surface area and microporosity, reaching values close to those of pure zeolite, while all materials exhibit the expected decrease in adsorption capacity with increasing temperature due to the

exothermic nature of the process. In addition, the structuring of these materials into fibers, membranes, and 3D-printed architectures demonstrates a clear trade-off between intrinsic capacity and process performance, since although electrospun membranes show lower adsorption capacity compared to powders due to the incorporation of polymeric components, they significantly improve mass transfer, reduce diffusion limitations, and enhance mechanical properties and handling, whereas 3D-printed structures further optimize flow distribution, reduce pressure drop, and enable better heat and mass transfer through designed porosity and geometry, making these structured adsorbents more suitable for practical applications in cyclic adsorption processes and highlighting the importance of coupling material composition with structural design to maximize overall efficiency [2-4].

Conclusions

The conclusions of this work demonstrate that geopolymer/zeolite 13X composites are promising adsorbent materials for CO₂ capture by combining low cost, sustainability, and competitive performance, where the incorporation of zeolite significantly enhances adsorption capacity due to increased surface area and microporosity, while although powder materials provide the highest intrinsic capacities they present limitations related to mass transfer and handling, thus structuring the materials into fibers, membranes, and 3D-printed architectures improves transport properties, reduces pressure drop, enhances regeneration efficiency, and facilitates integration into cyclic processes, ultimately highlighting that the combination of chemical design and

structural engineering is essential for the development of advanced adsorbents aimed at process intensification and efficient implementation of CO₂ capture and utilization technologies.

Acknowledgements

The authors appreciate the support from the project PID2021-126235OB-C32 funded by MCIN/AEI/10.13039/501100011033/ and FEDER funds, and the financial support of Fundación UNICAJA and Erasmus+ for H2EXCELLENCE.

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O28. O₂/O₃ Gas Separation Using MOR-40 Adsorbent

Inês Rodrigues^{1*}, Vítor J.P. Vilar¹, Alexandre F.P. Ferreira¹

¹ LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

* up201606838@up.pt

This work investigates O₂/O₃ gas separation using adsorption and an ozone-resistant adsorbent to concentrate ozone while enabling oxygen recycling to the generator. MOR-40 pellets were synthesized, characterized, and shown to be highly ozone-resistant. Binary (O₂/O₃) breakthrough tests confirmed strong ozone selectivity, demonstrating the suitability of MOR-40 for O₂/O₃ separation. Using the proposed PSA cycle, the study achieved its goal of enriching the ozone stream while recovering oxygen for reuse.

Introduction

Ozone is a powerful oxidant commonly employed in water and wastewater treatment applications. However, the efficiency of ozone generators is relatively low, typically producing an ozone stream with concentrations below 15 wt.% [1]. To address this issue, implementing O₂/O₃ gas separation via adsorption technology offers a viable solution for concentrating the ozone stream while enabling the recycling of oxygen back into the ozone generator. Therefore, this work aims to study the O₂/O₃ gas separation using synthesized MOR-40 pellets.

Experimental

Pellets were synthesized using zeolite MOR-40 (ratio SiO₂/Al₂O₃ of 40) as raw material, colloidal silica (25 wt.%) as the binder, and distilled water. The process involved mixing the binder with zeolite, extruding the paste, spheronizing the pellets, and calcinating them at 450 °C for 4 hours. The zeolite (in powder and pellet form) and the binder were characterized using N₂ adsorption at 77 K, CO₂ adsorption at 273 K, mercury intrusion porosimetry, helium pycnometry, X-ray diffraction, SEM/EDS analysis, and mechanical strength tests. The adsorption isotherms of O₂ were measured using a magnetic-suspension microbalance at 280 and 303 K, under pressures up to 5 bar. The Langmuir model was fitted by minimizing the sum of residuals with the Excel Solver tool. Single (O₂) and binary (O₂/O₃) breakthrough curve (BTC) experiments were performed in a lab-scale fixed-bed unit at two distinct temperatures (282 and 300 K). The BTCs and a PSA system for O₂/O₃ gas separation were simulated using the gPROMS software.

Results

The MOR-40 pellets were successfully developed and characterized, showing high resistance to ozone degradation, as evidenced by consistent and reproducible results across multiple trials.

For the binary (O_2/O_3) breakthrough experiments, four different ozone partial pressures were examined to achieve four ozone equilibrium points, as it is not possible to determine adsorption equilibrium isotherms for pure ozone. Figure 1 **a)** shows one of the ozone BTC obtained at 282K and the simulation results, and Figure 1 **b)** shows the ozone equilibrium points at room temperature (circle symbol) and at 282K (triangle symbol), along with the Extended Langmuir fitting. Analysis of Figure 1 **a)** shows two fronts related to the breakthrough of oxygen and ozone, with ozone having a slower front due to its preferential adsorption over oxygen.

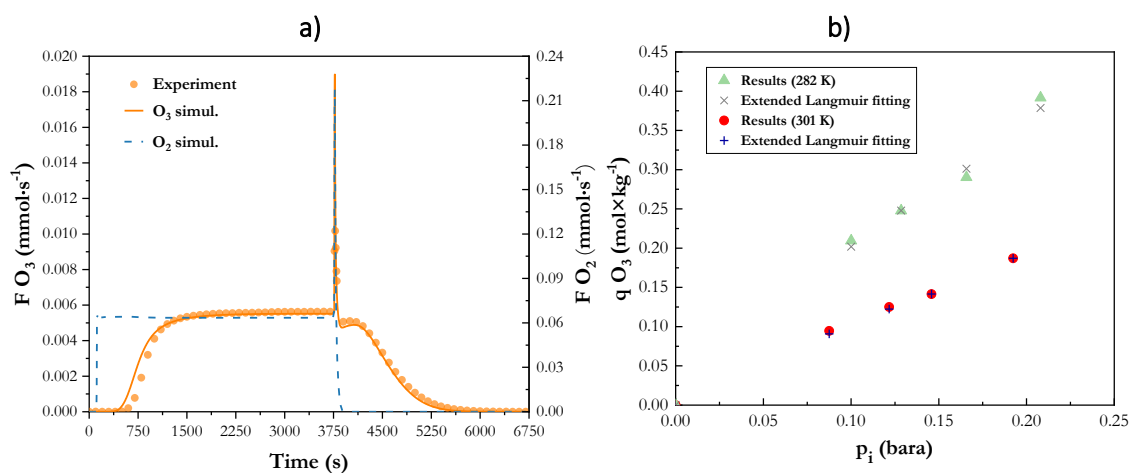


Figure 3. a) ozone BTC at 282K and the simulation results; b) ozone equilibrium points at room temperature (circle symbol) and at 282K (triangle symbol), along with the Extended Langmuir fitting.

A PSA cycle was simulated for O_2/O_3 gas separation, considering 4 steps: Feed (110s), Counter-Current Blowdown (60s), Counter-Current Purge (100s), and Counter-Current Pressurization (60s). The proposed PSA cycle can be extended to a triple-column unit, ensuring continuous feed consumption and production of both product streams. At 300 K and 2 bar, with a feed composition of 8% O_3 and 92% O_2 , the system achieved an O_2 purity of 99.96% and a recovery of 46.87%. For O_3 , the corresponding purity and recovery were 13.96% and 99.18%, respectively.

Conclusions

The MOR-40 pellets were developed and shown to have high resistance to ozone degradation, with consistent results across multiple trials. The analysis of the results indicated a distinct selectivity for ozone adsorption, with ozone molecules being preferentially adsorbed over oxygen molecules. Therefore, the synthesized MOR-40 pellets can be used effectively for O₂/O₃ separation. With the proposed PSA cycle, the main objective of the study was achieved: concentrating the ozone stream while simultaneously recovering oxygen, which can be recycled back to the ozone generator.

Acknowledgments

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O29. ENHANCED CO₂ ADSORPTION IN SYNTHESIZED CUBE-SHAPED ZEOLITE 4A FRAMEWORK.

Nisrine Jabli¹, Zineb Ouzrour¹, Abderrahman Mellalou^{*1}, Johan Jacquemin¹, Youssef Tamraoui¹ and Fouad Ghamouss^{*1}

¹ Materials Science, Energy and Nano-engineering department, Mohamed VI Polytechnique University Benguerir, Morocco

^{*} Fouad.ghamouss@um6p.ma, Abderrahman.Mellalou@um6p.ma

Summary of the work

This study addresses the urgent need for efficient and cost-effective CO₂ capture materials by exploring the synthesis of zeolite 4A using natural kaolin as a precursor. A highly crystalline Na-zeolite A framework was synthesized through a controlled hydrothermal process and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET) analyses. The CO₂ adsorption performance was investigated under varying temperatures and pressures. The synthesized NaA zeolite exhibited a maximum CO₂ uptake of 3.625 mmol g⁻¹ at -20 °C and 13 bar, surpassing previously reported values for zeolite 4A [1]. Equilibrium and thermodynamic studies confirmed the exothermic and spontaneous nature of the adsorption process, reinforcing the material's potential in sustainable CO₂ mitigation.

Introduction

The development of efficient and economically viable adsorbents is essential to address the increasing demand for CO₂ capture technologies. In this study, natural kaolin was explored as a low-cost aluminosilicate precursor for the hydrothermal synthesis of Na-zeolite 4A with enhanced CO₂ adsorption performance [1].

Experimental

A highly crystalline Na-zeolite A framework was synthesized through a controlled hydrothermal process using natural kaolin as the precursor. The synthesized material was characterized by XRD, SEM, FTIR, and BET analyses. CO₂ adsorption measurements were carried out under different temperatures and pressures, and the equilibrium data were analyzed using the Langmuir, Freundlich, and Sips isotherm models. Thermodynamic parameters were also determined to investigate the adsorption behavior [1].

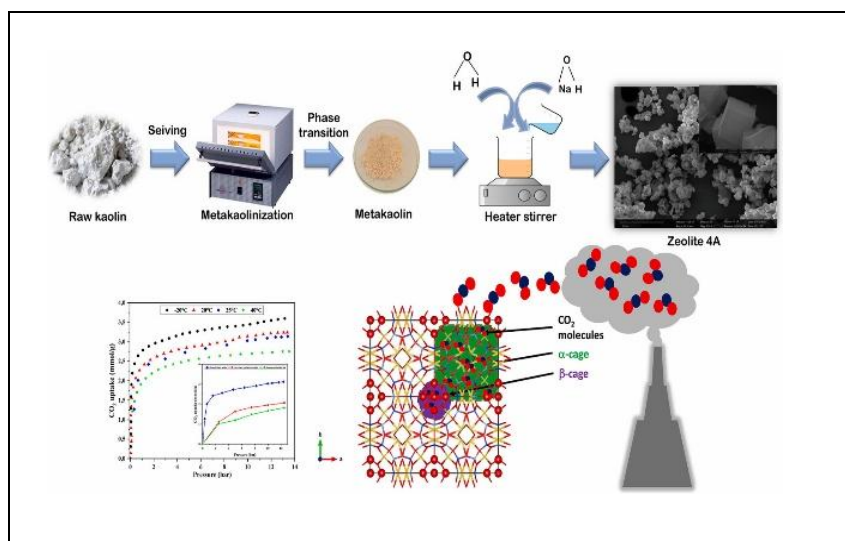
Results

The produced NaA zeolite exhibited a maximum CO₂ uptake of 3.625 mmol g⁻¹ at -20 °C and 13 bar, surpassing previously reported values for zeolite 4A, showcasing the material's enhanced adsorption capabilities [1]. The equilibrium data were fitted using Freundlich, Langmuir, and Sips isotherm models. Based on the coefficient of determination (R²), the Sips isotherm provided the best fit to the equilibrium data at different adsorption temperatures. Thermodynamic studies showed spontaneous and exothermic adsorption behavior, with $\Delta H = -18.385 \text{ kJ mol}^{-1}$, $\Delta S = -55 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta G = -4.471 \text{ kJ mol}^{-1}$ obtained at -20 °C. The combined isotherm and thermodynamic analyses confirmed the favorable adsorption behavior of the synthesized zeolite [1].

Conclusion

The hydrothermally synthesized Na-zeolite 4A derived from natural kaolin exhibited an excellent CO₂ adsorption performance, with favorable equilibrium and thermodynamic characteristics. These findings demonstrate the potential of this material as an efficient and cost-effective adsorbent for sustainable CO₂ capture.

Graphical abstract



Keywords

Zeolite 4A; Kaolin; Rietveld refinement; CO₂ capture; Porous material

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O30. Insights of rare earth elements recovery from acid mine drainages by adsorption onto clays minerals in SW Spain.

Aníbal López-Marín^{1,2*}, Rafael León Cortegano³, Rosa Martín-Rodríguez^{1,2}, Ana C. Perdigón^{1,2}, Carlos Ruiz Cánovas³

¹*Departamento de Química e Ingeniería de Procesos y Recursos (QUIPRE), Universidad de Cantabria, Av. de los Castros 46, 39005, Santander, Spain.*

²*Nanomedicine Group, Instituto de Investigación Marqués de Valdecilla (IDIVAL), Av. Cardenal Herrera Oria s/n, 39011, Santander, Spain.*

³*Departamento de Ciencias de la Tierra, Universidad de Huelva, Av. del Tres de Marzo s/n, 21071, Huelva, Spain.*

* *anibal.lopez@unican.es*

This study evaluates the capability of di- and trioctahedral clays to adsorb rare earth elements (REE) from acid mine drainage (AMD) generated in the Iberian Pyrite Belt. Montmorillonite, saponite, Laponite, and synthetic micas were exposed to AMD at pH 2.3–3.1 for up to 24 h. Clay structures remained mostly stable under acidic conditions, with montmorillonite showing the least structural damage according to XRD patterns. After partial neutralization and Fe removal, REE adsorption became significant, reaching up to 780 ppm in clay minerals and up to 50% removal efficiency. SEM analyses indicate REE incorporation through surface adsorption and co-precipitation, along with notable Cu and Fe uptake. Results highlight the potential of clay minerals as low-cost adsorbent materials for recovering critical elements selectively from AMD.

Introduction

In the province of Huelva (Andalusia, Spain), mining activity allocated within the Iberian Pyrite Belt (IPB) has intensified the generation of acid mine drainage (AMD), mainly due to the presence of mining tailings enriched in heavy metals, sulfides and iron as a by-product of the copper industry [1]. Therefore, acid mine drainage (pH 1.0 – 2.5) constitutes a latent risk to the environment, due to the possibility of infiltration and acidification of soils and water bodies.

Interestingly, authors have confirmed the presence of rare earth elements (REE) in significant concentrations in acid mine drainage [2]. The significant concentration of REE³⁺ in AMD supports the hypothesis of recovery of critical elements from secondary resources [3,4]. The aim of this research is the study of adsorption conditions for rare earth elements present in acid mine drainage from leaching processes of the Poderosa mine, located within the IPB in the province of Huelva, onto several clays. The REE adsorption mechanism is studied using di- and trioctahedral smectite clays and synthetic micas.

Experimental Methodology

For study of the adsorption of rare earth elements from acid mine drainage using clays, each clay sample (Montmorillonite SWy-2, Saponite Sumecton SA, Laponite RD and Na-micas) was placed in contact in a ratio of 100 mg of clay per 30 mL of AMD in a rotary shaker. The adsorption process was measured at different initial pH values (2.3, 3.1), previously neutralized with 0.1 M NaOH solution to prevent degradation of the clay structure under acidic conditions [5]. The contact time of the AMD–clay systems in batch mode was set at a maximum of 24 h, with 20 mL aliquots taken at times $t = 0.5, 1, 2, 4, 6$, and 24 h.

For treated acid mine drainage (TAMD), removal of excess Fe was eliminated by precipitation of ferric phase and filtration. After each batch, each suspension was centrifuged, separating the solid and drying at 50°C. The powder solid was subsequently studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). REE concentration were measured in the supernatant by optical emission spectroscopy (ICP-OES).

Results

Clay minerals exhibited distinct structural behaviors when are exposed to AMD, reflecting their di- and trioctahedral nature. XRD patterns indicates that all clays systems remained structurally stable at $\text{pH} < 3.1$, although trioctahedral saponite, Laponite, and high-charge micas have more noticeable laminar alteration than dioctahedral montmorillonite. This structural degradation is consistent with the modification of active surface sites under acidic conditions, potentially influencing the REE uptake and the stability of clays as time of contact increases.

After partial neutralization and Fe removal in TAMD, REE adsorption was noticeable, reaching up to 50% removal efficiency from the supernatant and a maximum capacity of 780 ppm onto clay minerals. Rapid adsorption occurred within the first 0.5 h of contact. SEM/EDS analyses confirmed that REE retention occurred through co-precipitation, particularly as phosphate phases on montmorillonite. Lower traces of U and Th were detected as presence of REE increases. In contrast, saponite and Laponite presumable favored surface adsorption due to their high specific surface area. Significant incorporation of Cu and Fe was also detected, including evidence of secondary formation such as pyrite and sulphates.

Conclusions

AMD–clay systems display adsorption behaviours strongly influenced by clay structure and contact time. Dioctahedral montmorillonite maintains higher structural integrity than trioctahedral saponite, Laponite, and Na-micas, which likely affects the availability

of active sites for REE uptake. Rapid adsorption occurs within the first 0.5 h, reaching maximum REE capacity near to 780 ppm. REE and U-Th retention appears to involve phosphate co-precipitation on montmorillonite surfaces, while saponite and Laponite could allow surface adsorption due to their high specific surface area. Cu and Fe also dominate competitive adsorption processes, occasionally leading to secondary mineral formation such as pyrite (FeS_2) and sulphates.

Acknowledgments

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O31. Engineering Organic-Inorganic Interfaces in Hybrid Nanomaterials for Visible-Light-Driven Environmental and Biomedical Applications.

Vesna Lazić^{1*}, Valentina Nikšić¹, Katarina Isaković¹, Miljana Dukić¹, Dušan Sredojević¹

¹ Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Center of Excellence for Photoconversion, University of Belgrade, Serbia.

* vesna.lazic@vin.bg.ac.rs

Summary

Organic-inorganic hybrid nanomaterials based on interfacial interactions between metal oxides and phenolic ligands represent a versatile platform for visible-light-driven environmental and biomedical applications. In this work, multifunctional hybrid systems composed of TiO₂, ZrO₂, ZnO, SiO₂, and Fe₃O₄ nanoparticles modified with redox-active organic molecules were investigated. Surface functionalization enabled the formation of interfacial charge transfer complexes, resulting in extended visible-light absorption, enhanced photocatalytic activity, and improved biological performance. The materials obtained demonstrated efficient degradation of organic pollutants, antimicrobial activity against bacteria and fungi, and successful immobilization of horseradish peroxidase while preserving catalytic stability. The results indicate that rational tailoring of the organic-inorganic interface can simultaneously control charge-transfer processes, reactive oxygen species generation, and enzyme-surface interactions. Such multifunctional systems represent promising candidates for sustainable hydrogen production, antimicrobial materials, and advanced bioactive platforms.

Introduction

Metal oxide nanoparticles are widely investigated due to their photocatalytic, optical, and antimicrobial properties. However, many conventional oxide systems exhibit limited visible-light activity and may show poor selectivity or insufficient biocompatibility. One promising strategy for overcoming these limitations is surface modification with phenolic and polyphenolic ligands that form interfacial charge-transfer complexes (ICTCs).

The formation of ICTCs can significantly modify the electronic and surface properties of metal oxides, thereby enabling visible-light activation and improving charge-separation efficiency. In addition, naturally derived ligands such as caffeic acid, gallic acid, salicylic acid, and 5-aminosalicylic acid introduce additional redox-active functionalities and improve interactions with biomolecules and microorganisms.

The aim of this work was to investigate the relationship between surface chemistry, interfacial charge-transfer processes, and multifunctional performance of hybrid

nanomaterials designed for photocatalytic hydrogen production, antimicrobial, and enzymatic applications.

Experimental

Hybrid nanomaterials were synthesized using TiO_2 , ZrO_2 , ZnO , SiO_2 , and Fe_3O_4 nanoparticles as inorganic supports. Surface functionalization was performed using selected phenolic and polyphenolic ligands through adsorption and coordination interactions at the oxide surface.

The obtained materials were characterized using UV–Vis diffuse reflectance spectroscopy, FTIR spectroscopy, X-ray diffraction, EPR spectroscopy, and thermal analysis. Photocatalytic performance was evaluated by hydrogen production experiments under UV and visible light irradiation.

Antimicrobial activity was tested against representative Gram-positive and Gram-negative bacterial strains, as well as fungal species. Enzyme immobilization experiments were performed with horseradish peroxidase as the model enzyme, and catalytic stability and reusability were monitored over multiple reaction cycles.

Results and Discussion

Surface modification of metal oxides with phenolic ligands resulted in pronounced changes in optical behavior, particularly in the visible region. UV–Vis analysis confirmed a redshift of the absorption bands, indicating the formation of interfacial charge-transfer complexes and an improved visible-light response.

Among the investigated systems, ZnO - and ZrO_2 -based hybrids exhibited enhanced photocatalytic hydrogen production under visible-light irradiation compared with pristine oxides. The improved activity was associated with ligand-to-metal charge-transfer processes, improved separation of photogenerated charge carriers, and enhanced utilization of visible-light energy.

The antimicrobial studies demonstrated that incorporating redox-active ligands significantly improved biological activity. Hybrid materials showed effective inhibition of both Gram-positive and Gram-negative bacteria, as well as fungal strains. In several TiO_2 - and SiO_2 -based systems, enhanced activity under visible-light irradiation suggested a significant contribution from photoinduced oxidative stress mechanisms.

Fe_3O_4 -based hybrid systems functionalized with amino- and carboxyl-containing ligands demonstrate efficient immobilization of horseradish peroxidase. The immobilized enzyme retained catalytic activity during repeated reaction cycles, indicating favorable enzyme-surface interactions and good operational stability.

The obtained results demonstrate that the interfacial chemistry between inorganic nanoparticles and organic modifiers plays a critical role in controlling photocatalytic efficiency, biological response, and catalytic stability.

Conclusions

Organic-inorganic hybrid nanomaterials based on interfacial charge-transfer interactions represent highly versatile, multifunctional systems. Surface engineering using phenolic ligands enables simultaneous tuning of optical, photocatalytic, antimicrobial, and enzymatic properties.

The investigated materials exhibited enhanced visible-light activity, improved antimicrobial performance, and efficient enzyme immobilization with preserved catalytic stability. These findings highlight the importance of rational interface design for the development of sustainable materials intended for environmental remediation, photocatalysis, and bioactive applications.

Acknowledgments

This work was supported by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia (Contract Number: 451-03-33/2026-03/200017)

O32. Stable Immobilization of Horseradish Peroxidase on Dopamine-Functionalized Fe₃O₄ Nanoparticles for Tetracycline Degradation.

Katarina Isaković^{1*}, Miljana Dukić¹, Dušan Sredojević¹, Milena Marinović-Cincović¹, Zorica Knežević-Jugović², Joaquin Silvestre-Albero³, Vesna Lazić¹

¹ Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Center of Excellence for Photoconversion, University of Belgrade, Serbia

² Faculty of Technology and Metallurgy, Department of Biochemical Engineering and Biotechnology University of Belgrade, Serbia

³ Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, San Vicente del Raspeig 03690, Spain

* katarina.isakovic@vin.bg.ac.rs

Summary

In this study, magnetite nanoparticles (Fe₃O₄) were functionalized with dopamine (DOP) to form interfacial charge transfer (ICT) complexes suitable for covalent enzyme immobilization. Dopamine strongly binds iron oxide through its catechol groups, while its amino group provides reactive sites for further bioconjugation. These ICT complexes modify the physicochemical and electronic properties of metal oxide surfaces, supporting catalytic and biotechnological applications. Horseradish peroxidase (HRP), an enzyme with high catalytic activity and broad environmental potential, was immobilized onto dopamine-functionalized Fe₃O₄ nanoparticles. Immobilization of the enzyme onto the magnetic support enhances the stability of the resulting composite and enables its potential recovery and reuse. The resulting biocatalyst was subsequently evaluated for its ability to degrade tetracycline, a widely used antibiotic frequently detected in wastewater. This approach enables efficient enzyme attachment, convenient magnetic separation, recovery, and potential reuse, offering a promising strategy for sustainable wastewater treatment.

Introduction

The increasing presence of antibiotic residues in aquatic environments has created a need for efficient and sustainable treatment methods. Tetracycline is a widely used antibiotic that is only partially metabolized and can enter wastewater, surface water, sediments, and soil. Its persistence may negatively affect ecosystems and contribute to the development of antibiotic-resistant bacteria. HRP is a promising biocatalyst for pollutant degradation because it operates efficiently under mild reaction conditions. However, the limited stability and recovery of free enzymes restrict their practical application. By selecting appropriate phenolic compounds as ligands, the nanoparticle surface can be functionalized with various functional groups tailored to the requirements of the intended application. This strategy significantly advances

photocatalytic and biomedical applications based on metal oxide nanomaterials. Dopamine was selected as a suitable ligand because it contains appropriate functional groups that enable strong binding to the Fe_3O_4 surface and subsequent enzyme immobilization. The resulting $\text{Fe}_3\text{O}_4/\text{DOP}/\text{HRP}$ system combines catalytic activity with convenient magnetic separation, improved reusability, and potential application in tetracycline removal from wastewater.

Experimental

Fe_3O_4 nanoparticles were synthesized using a co-precipitation method with ammonium hydroxide (NH_4OH) as the precipitating agent and subsequently functionalized with dopamine as the selected ligand. HRP was immobilized onto the functionalized nanoparticles using different support amounts (5, 10, and 20 mg) and initial enzyme concentrations ranging from 10 to $100 \mu\text{g mL}^{-1}$. The catalytic activity of immobilized HRP was evaluated by oxidizing pyrogallol in the presence of hydrogen peroxide (H_2O_2), with product formation monitored spectrophotometrically at 420 nm. For tetracycline degradation experiments, the reaction was initiated by adding H_2O_2 , and changes in tetracycline concentration were monitored spectrophotometrically over the wavelength range of 250-800 nm for 3h. The synthesized and functionalized nanoparticles were characterized by thermogravimetric analysis, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Experimental characterization was complemented by theoretical calculations based on density functional theory.

Results and Discussion

FTIR analysis confirmed the successful functionalization of Fe_3O_4 nanoparticles with dopamine. The spectra obtained indicated dopamine binding to the nanoparticle surface via its catechol groups, while the amino groups remained available for subsequent covalent enzyme immobilization. The immobilized HRP retained substantial catalytic activity over five consecutive reaction cycles, demonstrating the enhanced operational stability and reusability of the $\text{Fe}_3\text{O}_4/\text{DOP}/\text{HRP}$ composite. The preservation of enzymatic activity following repeated magnetic separation further confirmed the suitability of dopamine-functionalized Fe_3O_4 nanoparticles as support for enzyme immobilization. Moreover, the immobilized enzyme system successfully degraded tetracycline under different pH and temperature conditions. These findings indicate that the $\text{Fe}_3\text{O}_4/\text{DOP}/\text{HRP}$ composite maintains its catalytic performance across varying reaction conditions and has promising potential as a reusable biocatalyst for removing antibiotic contaminants from wastewater.

Conclusions

Nanoparticles are promising support for enzyme immobilization due to their high specific surface area, functionalization potential, and favorable interactions with enzymes. In this study, interfacial charge-transfer complexes were investigated as support for immobilization. HRP was successfully immobilized onto dopamine-functionalized Fe_3O_4 nanoparticles through covalent binding. The Fe_3O_4 support offers simple, reproducible synthesis and enables rapid magnetic separation from reaction mixtures. The resulting $\text{Fe}_3\text{O}_4/\text{DOP}/\text{HRP}$ nanobiocatalyst exhibited enhanced catalytic efficiency and retained substantial activity after five reuse cycles, confirming its stability and suitability for repeated biocatalytic processes. Overall, this system represents a practical and promising platform for enzyme immobilization and biotechnological applications.

Acknowledgments

This work was supported by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia (Contract Number: 451-03-33/2026-03/200017)

O33. Laminar Differential Pressure (DP) Flow Meter: Operating Principle and High-Accuracy Multi-Gas Calibration.

Rosetta Technology Solutions S.L.*

1 Rosetta Technology Solutions S.L., San Sebastián de los Reyes, Madrid, Spain.

* ventas@rosetta-technology.com

Differential pressure (DP) flow meters based on a laminar flow element (LFE) provide a fast and accurate method for measuring gas flow across a wide range of process conditions. This communication reviews the operating principle of laminar DP flow measurement, from turbulent-to-laminar flow conversion through the LFE to the application of the Poiseuille equation and density correction factors for standardized mass flow calculation, together with practical aspects of LFE design and maintenance. It also examines the Gas Select™ feature, which relies on pre-loaded, NIST-traceable three-dimensional gas property tables to maintain calibrated accuracy across more than 98 gases without a physical recalibration, and discusses how temperature and pressure coefficients and turndown ratio affect accuracy away from standard calibration conditions.

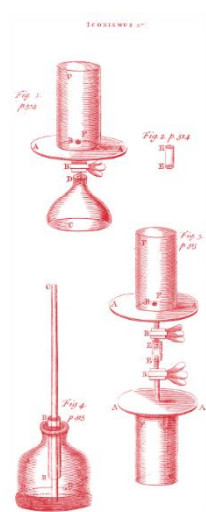


Figure 1- Apparatus for transference of gases and pressure gauge Credit: Wellcome Collection

Introduction

Differential pressure flow meters measure flow by monitoring the pressure drop generated across a restriction placed in the flow path. In 1992, laminar DP flow measurement was introduced as a refinement of this principle: incoming flow is first forced from a turbulent into a laminar regime before the pressure drop is measured,

which improves accuracy, response speed, and stability. This operating principle, together with the multi-gas capability enabled by Gas Select™, is directly relevant to processes that require frequent gas changes without loss of measurement accuracy.

Operating principle of laminar DP flow measurement

Laminar DP mass flow instruments combine a laminar flow element (LFE) with pressure and temperature sensing in four steps. First, the LFE's array of thin, parallel channels converts turbulent incoming flow into laminar flow.

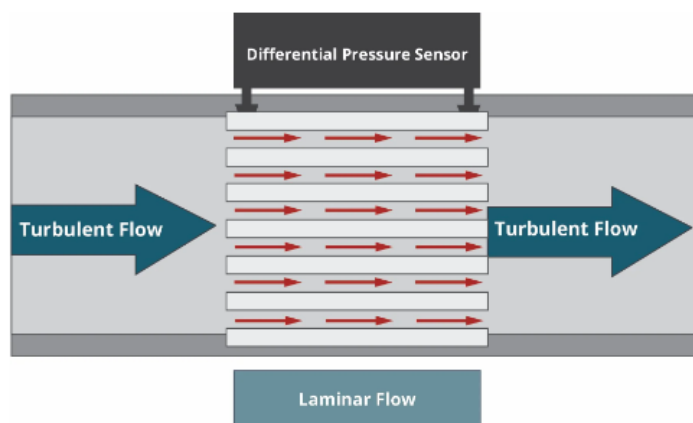


Figure 2- Turbulent incoming flow is converted into laminar flow by the LFE's array of thin, parallel channels.

This distinction is governed by the Reynolds number (Re): flow is considered laminar for $Re < 2000$ and turbulent for $Re > 2000$, and the LFE is designed to keep the flow within the laminar regime across its rated range.

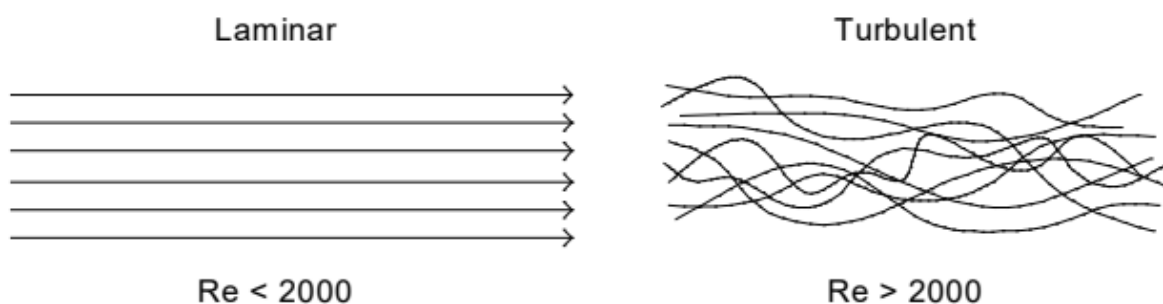


Figure 3 - Two Types of Flow

Second, a differential pressure sensor measures the pressure drop across the LFE, while absolute pressure and temperature sensors record the real-time conditions inside the

flow channel; the standard differential pressure sensor has a full-scale range of approximately 1 psi, although other ranges are available for specific configurations.

Third, the volumetric flow rate is calculated from the measured pressure drop and the fluid viscosity using the Poiseuille equation:

$$\text{Volumetric flow} = (P_1 - P_2) \cdot \pi \cdot r^4 / (8 \cdot \eta \cdot L) = K \cdot (\Delta P) / \eta,$$

where P_1 and P_2 are the static pressures at the inlet and outlet, r is the hydraulic radius of the restriction, η is the absolute viscosity of the fluid, L is the length of the restriction, and K is a constant that encompasses the geometric factors of the LFE.

Fourth, density correction factors for temperature (T_s/T_a), pressure (P_a/P_s), and compressibility (Z_s/Z_a) are applied to convert the volumetric flow into a standardized mass flow rate:

$$\text{Mass flow} = (\text{Volumetric flow}) \cdot (T_s/T_a) \cdot (P_a/P_s) \cdot (Z_s/Z_a).$$

LFE stack design and practical considerations

Physically, the LFE is built as a stack of thin, smooth, hard plates separated by very thin spacers, forming an array of narrow, elongated passages through which the gas is forced; because these passages are long and narrow relative to their cross-section, wall friction dominates the flow behavior, driving it into the laminar regime independently of the upstream flow condition. The number and size of these passages is sized during the design of each meter so that the expected flow range produces a pressure drop within the sensor's range; the resulting geometric constant K is specific to each meter model.

A direct practical consequence is that the narrow spacers also act as a coarse particulate trap: foreign material retained in the stack can change the effective flow area assumed constant since calibration and/or disturb the laminar regime, shifting the instrument's calibration over time. Maintaining clean, filtered process gas upstream of the LFE is therefore a practical requirement for preserving accuracy in service, not only at the time of calibration.

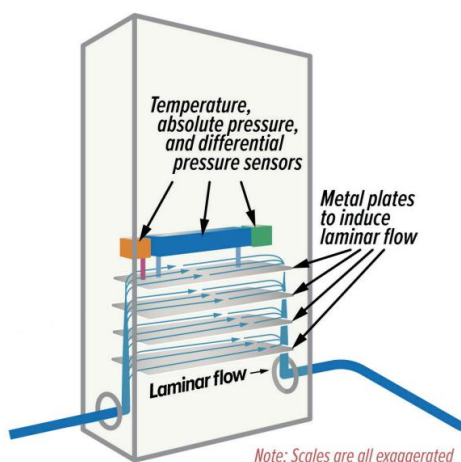


Figure 4 - Laminar differential pressure mass flow technology

Multi-gas accuracy through the Gas Select™ feature

Each Alicat laminar DP instrument is pre-loaded with three-dimensional, NIST-traceable gas property data (viscosity and compressibility as functions of pressure and temperature) for more than 98 gases.

Because the instrument reports pressure and temperature readings at high frequency and correlates them against the relevant gas table in real time, selecting a different gas in the Gas Select™ menu changes the referenced gas properties table without requiring any physical recalibration.

As a practical example, a device calibrated on argon maintains an accuracy of $\pm 0.6\%$ of reading or $\pm 0.1\%$ of full scale across different pressure and temperature conditions, and the same level of accuracy is preserved when the instrument is switched to air or to any other gas in the table, provided the correct gas is selected. This behavior has been validated against a NIST-traceable three-component gas mixture (12% CO₂, 7% O₂, 81% N₂) measured with an air-calibrated device, yielding a total measurement error of 0.15% of reading at full scale, within the published accuracy specification. This table-based method differs from the K-factor approach used in thermal mass flow technology, where a single conversion factor is applied to translate a reading calibrated on one gas to another; because K-factors are only accurate under the specific temperature and pressure conditions for which they were derived, operating away from those conditions reduces the accuracy of the corrected reading.

Accuracy under real operating conditions: temperature and pressure coefficients

Published accuracy specifications are normally referenced to a standard calibration condition, typically 25°C and atmospheric pressure, while actual process conditions

frequently differ from this reference. This deviation is commonly quantified through temperature and pressure coefficients, each expressing the additional mass flow span shift, as a percentage of reading, per unit change away from the calibration point.

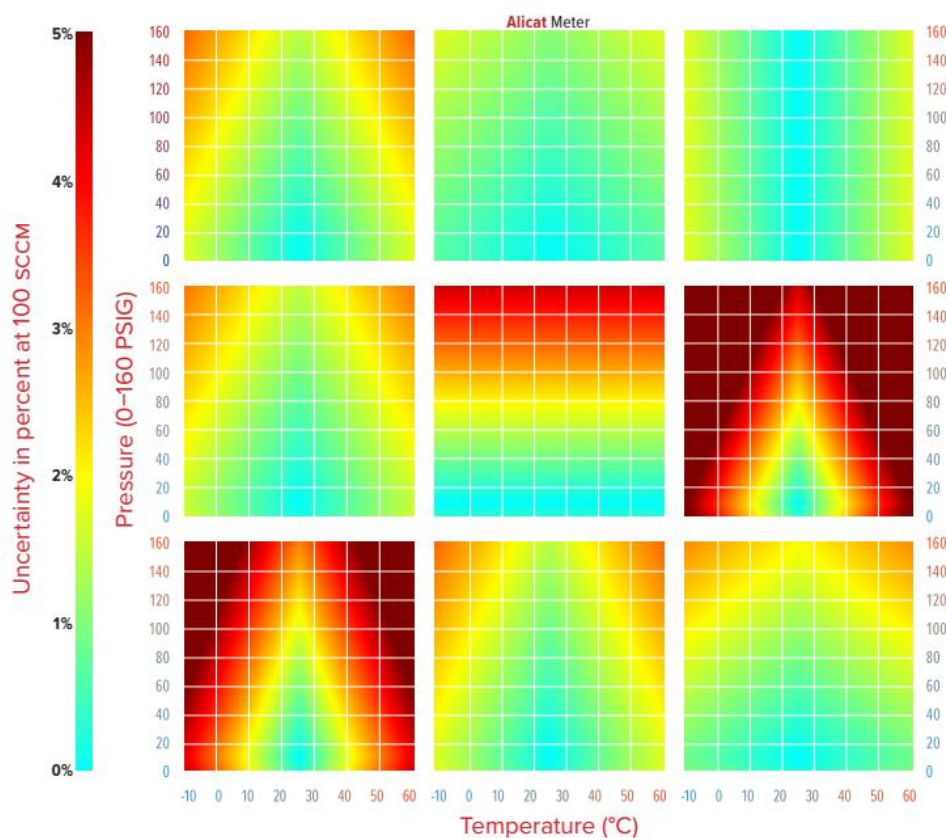


Figure 4 - Heat Maps Showing Uncertainty in Flow Measurement for Various Manufacturers

A related practical consideration is turndown ratio: because uncertainty at low flow is dominated by a fixed zero-point offset rather than a percentage of reading, the same absolute uncertainty becomes an increasingly large relative error as flow drops, so a specification expressed only as a percentage of full scale can understate the uncertainty at high turndown.

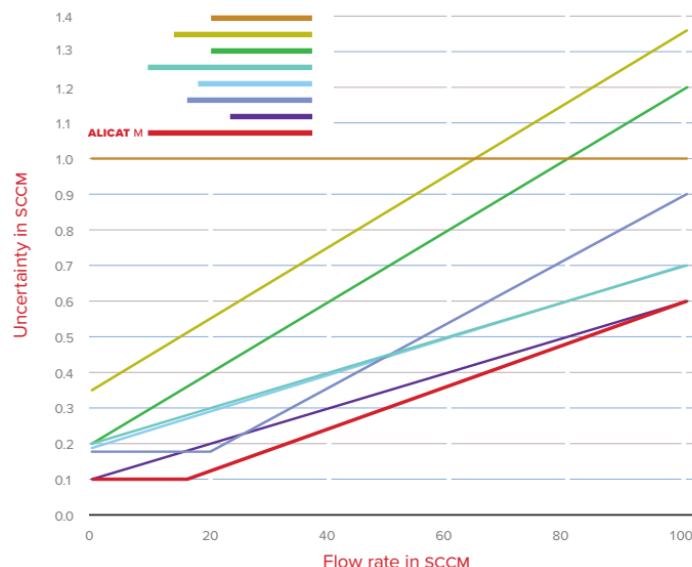


Figure 5 - Uncertainty Comparison: Flow Rate Error vs. Flow Rate for 100 sccm MFCs for Various Manufacturers

For an instrument whose gas data spans a wide pressure and temperature range, as with the 3D tables behind Gas Select™, this also explains why accuracy can remain stable away from the calibration point: the correction is looked up from measured data rather than extrapolated from a single-point calibration.

Conclusions

Laminar DP flow measurement combines a physically simple sensing principle — pressure drop across a laminar flow element, resolved through the Poiseuille equation and density correction — with pre-loaded, NIST-traceable multi-gas data tables accessed through Gas Select™. In practice, this allows a single instrument to measure or control more than 98 gases with consistent, NIST-traceable accuracy across changing process conditions, without the physical recalibration or condition-dependent accuracy loss associated with K-factor-based approaches. Sustaining this accuracy in service depends on two often overlooked factors: keeping the process gas clean enough to preserve the LFE's laminar geometry, and accounting for temperature/pressure coefficients and turndown ratio away from calibration conditions.

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O34. Towards using Polanyi's adsorption potential theory for predicting gas adsorption in nanomaterials.

Flavian Stavarache¹, Azahara Luna-Triguero^{2 3}, Sofia Calero^{1 3}, Hideki Tanaka⁴, Jose Manuel Vicent-Luna^{1 3*}

1 Materials Simulation & Modeling, Department of Applied Physics and Science Education, Eindhoven University of Technology, P.O. Box 513, Eindhoven, 5600 MB, The Netherlands

2 Energy Technology, Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, Eindhoven, 5600 MB, The Netherlands

3 Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, P.O. Box 513, Eindhoven, 5600 MB, The Netherlands

4 Institute for Aqua Regeneration (ARG), Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan

**j.vicent.luna@tue.nl*

Assessing gas adsorption properties of nanoporous materials efficiently and cost-effectively is critical for applications such as carbon capture. In this work, we present a novel method based on Polanyi's adsorption potential theory, combined with an adapted thermodynamic model, to rapidly generate multiple adsorption isotherms from a single experimental or simulated isotherm. By making use of temperature-independent characteristic curves, which are alternative isotherm representations, this approach enables the prediction of isotherms at temperatures up to 100 K above the reference point. Validated against both simulated and experimental data, the method demonstrates high accuracy. Additionally, we explore an alternative approach for generating characteristic curves directly from the potential energy surface of a given adsorbent. This work advances scalable and accurate adsorption analysis for nanoporous materials.

Methodology

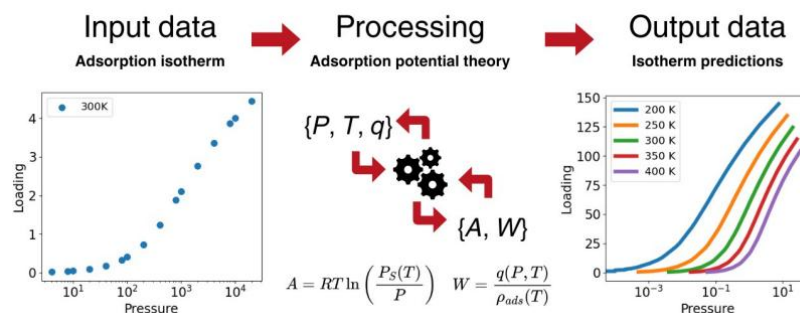


Figure 1. Proposed workflow of processing simulated or experimental single isotherms to generate isotherms at many different temperatures using Polanyi's adsorption potential theory.

Figure 1 summarizes the proposed workflow: a single adsorption isotherm is converted into a temperature-independent characteristic curve (adsorbed volume W vs. adsorption potential A), which can then be reconverted into an isotherm at a different temperature. Repeating this step for multiple temperatures yields the complete adsorption landscape. The workflow was validated using simulated and experimental adsorption isotherms of a combination of different adsorbents and adsorbates. This validation showed that isotherms measured at 300 K can be used to accurately predict isotherms in the 273–373 K range [1]. Applied to experimental isotherms, the method achieved equally strong agreement between predictions and measurements [1]. While Polanyi's adsorption potential is already established, it requires two gas properties: saturation pressure and adsorbed-phase density. Our approach introduces two novelties. First, we propose an adapted thermodynamical model to obtain the aforementioned gas properties, which outperforms previously used methods. Second, to validate the thermodynamical model, we developed an open source code, called RETMAP [2], which implements the complete theoretical framework, enabling isotherm predictions in seconds [1].

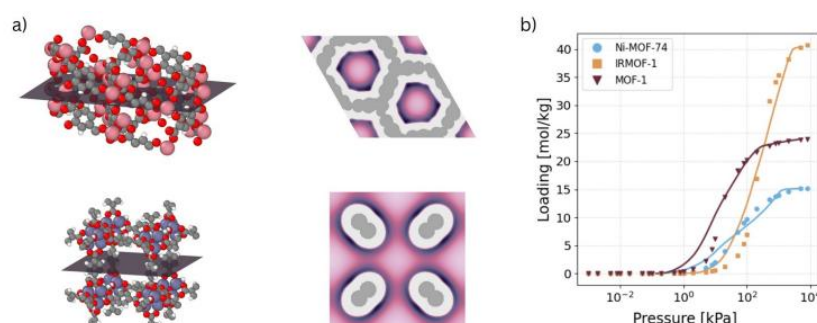


Figure 2. (a) Scans of the potential energy surface for Ni-MOF-74 and IRMOF-1, with the corresponding slices used; (b) argon adsorption at critical temperature; coloured line represents

the isotherm computed using the potential energy surface, marked lines represent the isotherms obtained from GCMC simulations.

While the aforementioned workflow can generate new isotherms quickly, it still requires an initial isotherm. To circumvent this and speed up material discovery, we explore a new method to generate characteristic curves directly from the pore environment and potential energy surface of nanoporous materials (Figure 2.a), bypassing expensive GCMC simulations. Figure 2.b demonstrates that this approach generates adsorption isotherms comparable to GCMC results at a fraction of the computational cost.

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O35. SODIUM POLY(HEPTAZINE IMIDE)-BASED ADSORBENTS FOR CO₂ CAPTURE.

Pedro Ouro^{1,2}, Daniel Pereira¹, Mariana Sardo¹, Igor Krivtsov², Ildefonso Marin-Montesinos¹, Luís Mafra¹, and Marina Ilkaeva^{2*}

¹University of Aveiro, Department of Chemistry, CICECO - Aveiro Institute of Materials, Aveiro, Portugal

²University of Oviedo, Department of Chemical and Environmental Engineering, Oviedo, Spain
*ilkaevamarina@uniovi.es

Sodium poly(heptazine imide) (NaPHI), a microporous polymeric carbon nitride, was investigated as a CO₂ adsorbent. Its crystallinity, tuned by thermal treatment, directly governs adsorption performance, reaching up to ca. 4 mmol/g with high CO₂/N₂ selectivity. NaPHI matches Zeolite 13X at room temperature and nearly doubles its capacity at 100 °C (ca. 2.1 vs. 1.1 mmol/g), making it attractive for flue-gas capture. To understand the adsorption mechanism, solid-state NMR (ssNMR) and X-ray absorption spectroscopy (XAS) were applied. ¹³C CP-Kinetics and Torchia, and 2D ¹³C–¹H HETCOR experiments using isotopically labelled ¹³CO₂ revealed that CO₂ capture in NaPHI operates through two simultaneous mechanisms: physisorption within the microporous channels, and reversible chemisorption via carbamic acid formation. These atomic-level insights provide a clear basis for the rational design of improved PHI-based CO₂ adsorbents.

Introduction

A new class of PCNs, the PHIs, has shown great potential for CO₂ capture. PHIs are attractive due to their (i) cost-effectiveness, (ii) thermal stability up to 450 °C, and (iii) moisture resistance, properties that distinguish them from metal-organic frameworks (MOFs), which are prone to structural collapse upon humidity exposure. PHIs can be synthesized rapidly and feature a microporous structure with an initial CO₂ adsorption capacity of approximately 4 mmol/g, competitive with Zeolite 13X. Despite these advantages, the semi-crystalline nature of PHIs has hindered mechanistic understanding of their CO₂ adsorption behavior. Thus, ssNMR and XAS were employed. ssNMR probed local carbon environments and adsorbate–adsorbent interactions, while XAS revealed the effect of CO₂ on the structural cations and their coordination environment. Together, these techniques provide atomic-level insight into CO₂ capture in NaPHI and lay the groundwork for next-generation PHI-based adsorbents.

Results and discussion

PXRD data (Figure 1A) show that NaPHI evolves from an amorphous PCN-like precursor into a crystalline material with increasing thermal treatment time. The prominent peak

at $8.2^\circ 2\theta$ indicates high intralayer order. Preliminary thermogravimetric CO₂ adsorption studies (Figure 1B) demonstrate that crystallinity directly correlates with adsorption capacity, with the fully crystalline NaPHI reaching ~ 3.0 mmol/g. ¹³C CP/MAS and HPDEC ssNMR spectra (Figure 1C) reveal three distinct carbon environments in NaPHI, which differ markedly from those reported for CaPHI by Burrow et al., suggesting that structural differences between these PHI variants may have significant implications for CO₂ capture performance. Porosity characterization via H₂ isotherms at -196°C confirmed NaPHI's (ultra)microporous character, with pore sizes of 0.33 and 0.47 nm. CO₂ and N₂ isotherms at 25°C yield adsorption capacities of 3.8 and 0.3 mmol/g, respectively, demonstrating high CO₂/N₂ selectivity.

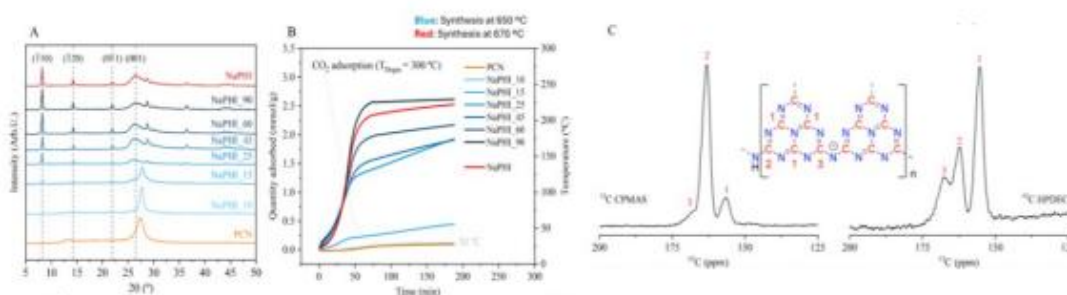


Figure 1 - (A) PXRD patterns; (B) CO₂ adsorption curves; (C) ssNMR

Temperature-dependent adsorption studies (Figure 2A) show that NaPHI matches Zeolite 13X performance at 30°C (ca. 3.0 mmol/g, 100% CO₂) and significantly outperforms it at elevated temperatures, at 100°C , NaPHI achieves 2.1 mmol/g versus only 1.1 mmol/g for Zeolite 13X, making it particularly suited for flue-gas carbon capture applications. Cyclic adsorption tests at 100°C (Figure 2B) confirm regenerability over multiple cycles. in situ PXRD revealed that pre-treatment temperature critically governs NaPHI's structural features and, consequently, its CO₂ uptake. ssNMR and XAS were then used to elucidate the adsorption mechanism at the atomic scale. ¹³C CP kinetics and Torchia experiments, performed under He and CO₂ atmospheres, revealed that CO₂ adsorption induces significant changes in the cross-polarization build-up times (TIS) at C1 and C3 carbon sites, while C2 remains largely unaffected, consistent with CO₂ interacting preferentially near the $-\text{NH}-$ bridging sites of the heptazine framework. Definitive evidence for dual adsorption was provided by ¹³C–¹H HETCOR experiments using isotopically labelled ¹³CO₂, which simultaneously identified: (i) physisorbed CO₂ (ca. 125 ppm, ¹H ~ 5 ppm), interacting weakly with pore-confined species; and (ii) chemisorbed CO₂ (ca. 158–162 ppm, ¹H > 10 ppm), assigned to carbamic acid/carbamate species formed by reversible covalent reaction of CO₂ with framework $-\text{NH}-$ bridges.

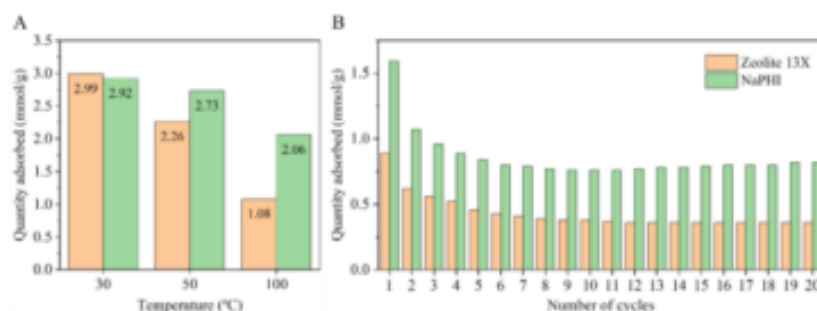


Figure 2 - (A) CO₂ adsorption at 3 temperatures; (B) CO₂ cyclic adsorption at 100 °C

Conclusions

NaPHI emerges as a highly effective CO₂ adsorbent whose performance is strongly governed by its structural order. Thermal treatment drives the formation of a crystalline NaPHI phase with well-aligned PHI layers, creating (ultra)microporous channels that enhance CO₂ adsorption capacity. Increased crystallinity correlates directly with higher adsorption capacities, reaching up to ca. 4 mmol/g and showing high selectivity for CO₂. Compared to the Zeolite 13X, NaPHI displays comparable performance at rt and superior CO₂ adsorption capacity at 100 °C, highlighting its potential for flue-gas carbon capture. in situ PXRD, ssNMR, and XAS reveal that temperature-dependent structural changes and specific framework–CO₂ interactions are key to its adsorption behavior, offering new insights into ways of further optimizing PHI-based materials for CO₂ capture.

O36. New methods for understanding and handling sorbed water

Yassin H. Andaloussi

Surface Measurement Systems Ltd, London, UK

Water plays an important role in many processes involving sorption, from atmospheric water harvesting, carbon capture, sorption heat pumps, indoor air quality remediation, catalysis and more. Water sorption, desorption, co-sorption, its kinetics and molecular state within sorbents are therefore pertinent topics where there are still many open questions and methodological challenges.

In this work we attempt to tackle some of these challenges through the use of advanced method and instrumental developments. The state of water within the pores will be investigated using ON-DVS (Operando NMR relaxometry dynamic vapour sorption), a method that enables bench-top coupled determination of sample vapour uptake at precise gas-phase concentrations with sub-microgram resolution, alongside recording T1/T2 relaxation times of the pore-enriched phase throughout. We also explore a method of rapid isotherm determination using non-equilibrium ramping experiments allowing for high throughput measurements for efficient material screening.

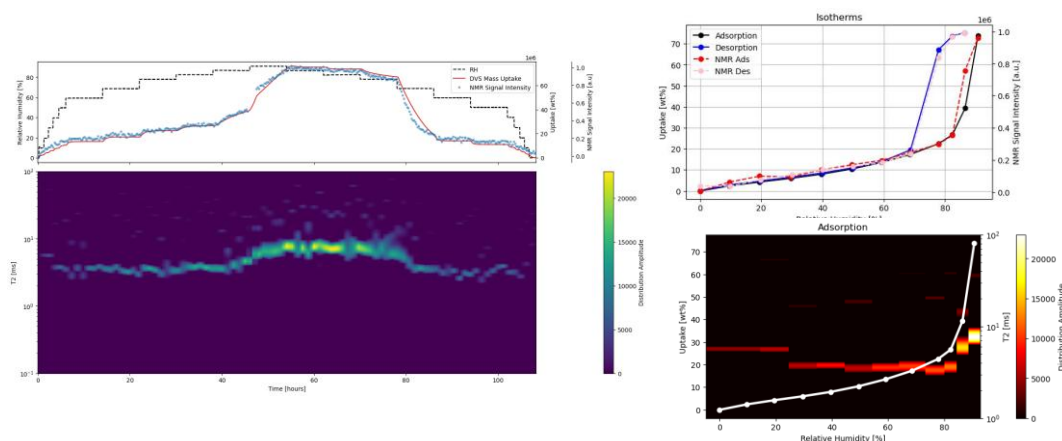


Figure 1. Gravimetric kinetics measurements and isotherms .

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Poster Communications

P01. Interacciones gas sólido mejoradas en Ni URJC 3 para la adsorción de H₂ y CO₂

Gisela Orcajo^{1*}, Elena García-Rojas¹, Jesús Tapiador¹, Carmen Martos¹, Pedro Leo¹

¹ Grupo de Ingeniería Química y Ambiental, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, España

* e-mail: gisela.orcajo@urjc.es

Resumen

En este trabajo se presenta Ni-URJC-3, un nuevo material metal-orgánico (MOF) basado en níquel diseñado para la adsorción de hidrógeno y dióxido de carbono. El material se sintetizó empleando el ligando tetratópico 5,5'-(diazene-1,2-diyl)diisotáltico (H₄ABTC), cuyo grupo azo (–N=N–) actúa como sitio básico de Lewis, favoreciendo interacciones más fuertes entre los gases y la estructura. A pesar de su área superficial moderada (158 m² g⁻¹), Ni-URJC-3 muestra un comportamiento sobresaliente en la adsorción de hidrógeno, alcanzando 3,7 % en peso a 77 K y 16 bar, así como una capacidad volumétrica de 59,5 g L⁻¹, valores cercanos a los objetivos del DOE para almacenamiento de H₂. En cuanto al CO₂, las isothermas a 273 K y 298 K muestran una entalpía de adsorción elevada (35,8 kJ mol⁻¹), indicativa de interacciones huésped-estructura intensas. Estos resultados posicionan a Ni-URJC-3 como un material prometedor para aplicaciones de almacenamiento y captura de gases, combinando afinidad química y efectos de confinamiento en su red microporosa.

Introducción

La transición hacia sistemas energéticos sostenibles requiere materiales capaces de almacenar hidrógeno de forma segura y eficiente, así como de capturar CO₂ con alta afinidad y regenerabilidad. El hidrógeno, considerado un vector energético clave, exige materiales con elevadas capacidades gravimétrica y volumétrica, mientras que la captura de CO₂ demanda sólidos con entalpías de adsorción suficientemente altas para garantizar una retención efectiva [1-3]. Los Metal–Organic Frameworks (MOFs) destacan por su elevada porosidad, modularidad estructural y posibilidad de incorporar grupos funcionales que modulan la interacción gas-sólido [4]. En este contexto, se ha desarrollado Ni-URJC-3, un MOF basado en níquel y un ligando azo que, según estudios previos, puede incrementar la afinidad por gases mediante interacciones específicas de tipo Lewis [1].

Experimental

Ni-URJC-3 se sintetizó mediante un procedimiento solvotérmico en DMF empleando H_4ABTC y nitrato de níquel, obteniéndose cristales adecuados para difracción de monocristal. La estructura reveló nodos Ni_2O_{11} conectados por ligandos $ABTC^{4-}$ formando una red tridimensional con canales microporosos [1]. La caracterización textural se realizó mediante isothermas de adsorción de argón a 87 K, obteniéndose un área BET de $158\text{ m}^2\text{ g}^{-1}$ y un volumen de poro de $0,074\text{ cm}^3\text{ g}^{-1}$. Las isothermas de H_2 se midieron a 77 K y 87 K en un analizador gravimétrico y volumétrico, mientras que las de CO_2 se registraron a 273 K y 298 K. Las entalpías de adsorción se calcularon mediante la ecuación de Clausius-Clapeyron [3].

Resultados

La estructura de Ni-URJC-3 presenta cavidades microporosas donde los grupos azo contribuyen a intensificar las interacciones gas-sólido. Aunque su área superficial es moderada, el material muestra un comportamiento excepcional en la adsorción de hidrógeno. A 77 K y 16 bar (Fig. 1), alcanza 3,7 wt%, superando a otros MOFs con áreas superficiales mucho mayores, como ZIF-8, MIL-100(Fe) o MOF-74(Mg), cuyos valores típicos oscilan entre 2,5 y 3,3 wt% [1]. La capacidad volumétrica total de $59,5\text{ g L}^{-1}$ se aproxima al objetivo del DOE (40 g L^{-1}), lo que resulta notable considerando la presencia de moléculas de DMF coordinadas que limitan parcialmente la accesibilidad del poro [2]. Este rendimiento se atribuye al efecto de confinamiento en cavidades estrechas y a la presencia simultánea de sitios ácidos (Ni^{2+}) y básicos ($-N=N-$), que favorecen la polarización de H_2 .

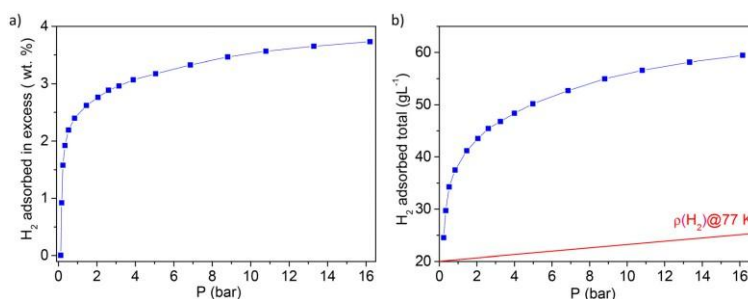


Figura1. Isothermas de adsorción de hidrógeno en exceso en base gravimétrica (a) y densidad de almacenamiento volumétrico (b) a 77K empleando el material Ni-URJC-3.

En cuanto al CO_2 , Ni-URJC-3 presenta una entalpía de adsorción de $35,8\text{ kJ mol}^{-1}$, superior a la de muchos MOFs convencionales ($20\text{--}30\text{ kJ mol}^{-1}$), lo que confirma una fuerte afinidad química [3]. Las isothermas muestran una adsorción más pronunciada a bajas presiones, coherente con la presencia de sitios de adsorción de mayor energía (ver Fig. 2).

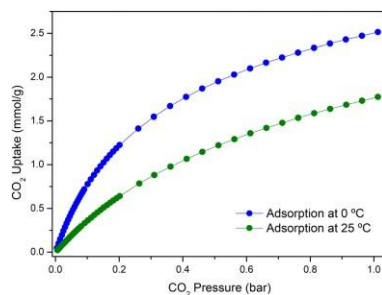


Figura 2. Isotermas de adsorción de CO₂ de Ni-URJC-3 a 0 y 25 °C.

En conjunto, los resultados demuestran que Ni-URJC-3 combina interacciones químicas específicas y microporosidad efectiva, logrando un rendimiento competitivo en adsorción de H₂ y CO₂ incluso frente a materiales con mayor área superficial.

Agradecimientos

Los autores agradecen sinceramente el apoyo financiero del Ministerio de Ciencia e Innovación de España (MCIN) y de la Agencia Estatal de Investigación (AEI) al proyecto ECOCAT (PID2022-136321OA-C22).

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P02. Textural and Surface Chemistry Effects on CO₂/CH₄ Separation: A Comparative Analysis of Five Commercial Clays.

Giselle I. Autié Castro^{1*}, Enrique Rodríguez-Castellón^{2,3*}, Juan A. Cecilia^{2,3}, D. Ballesteros-Plata^{2,3}, A. Infantes-Molina^{2,3}, Tania Farías¹

¹*Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, Zapata y G, Plaza de la Revolución, 10400, La Habana, Cuba.*

²*Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071 Malaga, Spain*

³*Instituto Interuniversitario de Investigación en Biorrefinerías (I3B), Facultad de Ciencias, Universidad de Malaga, Campus de Teatinos s/n, 29071 Malaga, Spain*

* *gautie@imre.uh.cu, giselleautie@gmail.com, castellon@uma.es*

This study explores the separation of methane (CH₄) and carbon dioxide (CO₂) at 25 °C using a series of clay minerals: sepiolite, saponite, palygorskite, montmorillonite, and kaolinite. Experiments were conducted using inverse gas chromatography (IGC), complemented with previously reported characterization data. Nitrogen adsorption at –196 °C was also incorporated to relate textural properties to the obtained adsorption heat values. The results revealed that all clays, except kaolinite, exhibited optimal separation of the CO₂/CH₄ mixture. The adsorption heats of both probe molecules, obtained from the IGC data, correlated with the surface chemistry and structural features of the clays. Nitrogen adsorption provided insights on surface area and porosity, which were essential for interpreting the separation behavior. The analysis highlights how variations in surface functional groups and textural characteristics influence the strength of the gas–solid interactions, determining the efficiency of CO₂/CH₄ separation.

Introduction

Clay minerals are naturally occurring aluminosilicates widely distributed in the Earth's crust, whose structural diversity and surface reactivity have enabled their use in a broad range of applications [1,2]. On the other hand, the separation methane (CH₄) and carbon dioxide (CO₂) mixtures is a key challenge in natural gas purification and biogas upgrading [3,4]. This study presents a comparative evaluation of CO₂/CH₄ separation using five commercial clays minerals with different structural features: saponite, palygorskite, sepiolite, montmorillonite, and kaolinite. The results are discussed in terms of the structural characteristics governing the separation capacity of the evaluated clays, integrating their textural properties with their overall separation performance. Experimental data were collected through Inverse Gas Chromatography (IGC), an advanced methodology that allows for the precise evaluation of adsorption behavior

and separation performance under dynamic flow conditions [5]. All data collected were obtained at 25 °C.

Results

Marked differences in the separation performance of the evaluated clay materials were observed. The variations in elution times reflect both the quadrupole moment of the probe molecules and the chemical and textural features of the materials. The adsorption heats and separation factors calculated for the studied samples are summarized in Table 1. Both components of the mixture were successfully resolved in four of the five materials evaluated. In all cases, CO₂ exhibited stronger interactions than CH₄, as evidenced by the longer retention times and interaction parameters. This behavior is consistent with the intrinsic physicochemical properties of the molecules: CO₂ has a significant quadrupole moment and greater polarizability, promoting stronger electrostatic interactions with charged surfaces and exchangeable cations, whereas CH₄ interacts mainly through weak dispersive forces. As expected, kaolinite showed no appreciable separation capability. The mixture did not resolve under the working conditions employed, since both components eluted overlapping.

Among the materials evaluated, saponite exhibited the highest separation factor ($\alpha = 15.6$), demonstrating superior selectivity for CO₂ compared to CH₄. This response is consistent with its well-developed microporous structure and relatively high specific surface area. The smectitic layered structure of saponite provides accessible interlayer spaces that enhance confinement effects and strengthen quadrupole interactions between CO₂ molecules and the clay surface. This interpretation is supported by the higher adsorption heat obtained for CO₂ ($Q_d = 27.2 \text{ kJ mol}^{-1}$), indicating stronger adsorbate–adsorbent interactions compared to the other clays.

Table 1- Obtained adsorption heat (Q_d) and separation factors values (α) for CH₄ and CO₂ adsorption in saponite, palygorskite, sepiolite and montmorillonite calculated from IGC data.

Sample	$Q_d \text{ CH}_4$ (kJ mol ⁻¹)	r^2	$Q_d \text{ CO}_2$ (kJ mol ⁻¹)	r^2	α
Saponite	16.3	0.9976	27.2	0.9807	15.6
Palygorskite	15.4	0.9957	26.2	0.9992	12.3
Sepiolite	15.1	0.9979	25.5	0.9993	2.0
Montmorillonite	15.6	0.9910	21.6	0.9845	6.7

Conclusions

Inverse gas chromatography (IGC) under dynamic conditions was used to evaluate the CO₂/CH₄ separation at 25 °C in five commercial clays (saponite, palygorskite, sepiolite, montmorillonite, and kaolinite). Kaolinite exhibited no detectable separation under

these conditions, consistent with its low specific surface area and microporosity. Adsorption heats confirm that CO₂ interacts with higher energy than CH₄ in all materials studied. However, CO₂/CH₄ selectivity depends on the combination of microporosity and surface chemistry. Saponite and palygorskite had the highest Q_d (CO₂) values and the best separation factors. In contrast, sepiolite showed low discrimination ($\alpha \approx 2$) due to its predominance of mesopores and adsorption in less confined domains, despite its high absolute capacity. The differences observed in Q_d (CO₂) (21–27 kJ mol⁻¹) are sufficient to explain the variations in α and should be considered when comparing materials.

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P03. Adsorptive Desulfurization of Diesel Fuel over Palygorskite Clay

Anne B. F. Câmara¹, Rafael V. Sales¹, João V. G. Souza¹, Aisha V. S. Pereira¹, Luiz C. Bertolino², Leila Campos⁴, Daniel Plata-Ballesteros², Enrique Rodríguez-Castellón³, Luciene S. de Carvalho¹

¹ *Institute of Chemistry, Federal University of Rio Grande do Norte, Energetic Technologies Research Group, 59078-900, Natal, Brazil.*

² *Mineral Technology Center, 21941-908, University City, Rio de Janeiro, Brazil.*

³ *Dpto. de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071, Málaga, Spain*

⁴ *Postgraduate Program in Chemistry - PPGQ, Federal University of Bahia, Salvador 40170-110, Brazil*

* E-mail address: luciene_car@hotmail.com

Palygorskite (Pal), a low-cost clay mineral, was investigated as a material for the adsorptive desulfurization of commercial diesel. The chemical activity of the surface was crucial for adsorption via π -complexation with Fe species. The results showed a correlation with the pseudo-second-order kinetic model ($R^2 > 0.99$), suggesting chemisorption as the rate-determining step. The maximum adsorption capacity calculated from the Langmuir isotherm was $6.25 \text{ mg} \cdot \text{g}^{-1}$ at 318 K. The material stands out for being abundant in nature, environmentally friendly, and promising for application in adsorption and catalysis processes.

Introduction

Palygorskite (Pal) is a hydrated magnesium aluminum silicate with fibrous morphology, high porosity, and active surface groups. Its use in sulfur adsorption from diesel oil is a recent approach to reducing the production of sulfur oxides (SO_x), which are harmful to human health. Environmental regulations require ultra-low sulfur levels (10-15 ppm), necessitating the search for low-cost adsorbents compared to hydrodesulfurization (HDS) treatment. Thus, Pal was employed as a potential adsorbent for desulfurization.

Experimental

Samples were subjected to wet grain size classification ($< 20 \text{ } \mu\text{m}$) and magnetic separation (15 kGauss). Characterization included XRF (EDX-720/800HS), XRD (Rigaku Miniflex II), and XPS (Physical Electronics PHI 5700). Adsorption assays utilized 8 mL of diesel and 0.3 g of adsorbent under stirring, varying temperature, time, and adsorbate concentration according to the specific method. Sulfur quantification was performed by ultraviolet fluorescence (UVF) spectrometry following the ASTM D5453 standard.

Results and discussion

The chemical composition of Pal obtained by XRF indicates a predominance of SiO_2 (58.99%), Al_2O_3 (15.70%), Fe_2O_3 (12.45%), and MgO (4.70%). XPS analysis (Fig. 1a) revealed Fe(0), Fe(III), and FeOOH species at 709.1, 712.4, and 715 eV, respectively (Fig. 1b), evidencing a strong interaction between Fe^{3+} ions and thiophenic aromatic rings via π -complexation. The XRD diffractogram (Fig. 1c) confirmed the presence of palygorskite and quartz (ICSD Nos. 01-082-1873 and 01-085-0794).

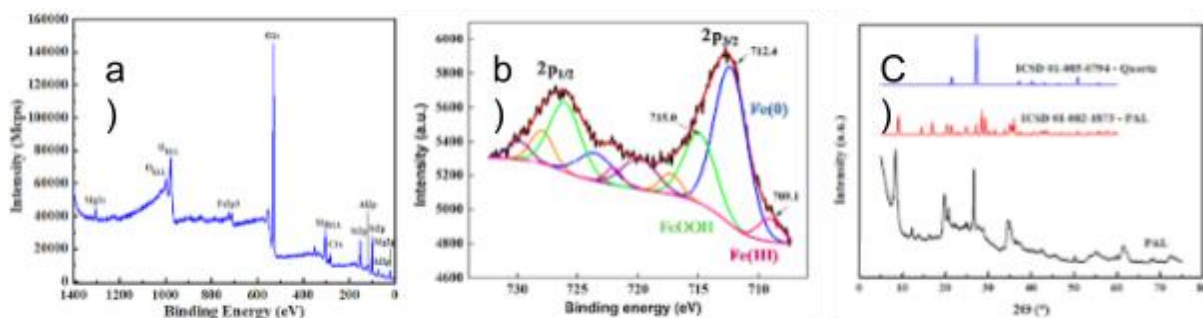


Figure 1.

Kinetic data fit the pseudo-second-order model ($R^2 = 0.99$), with experimental ($1.94 \text{ mg}\cdot\text{g}^{-1}$) and calculated ($1.95 \text{ mg}\cdot\text{g}^{-1}$) q_e values being very close, indicating chemisorption as the dominant mechanism. Regarding the thermodynamic parameters, the standard Gibbs free energy (ΔG°) showed values of 6.02, 4.00, and 1.84 kJ/mol for temperatures of 298 K, 308 K, and 318 K, respectively. The standard enthalpy change (ΔH°) was

44.73 kJ/mol, while the standard entropy change (ΔS°) presented values of 42.35, 47.52, and 52.843 J/K·mol across the tested temperatures. These results indicate an endothermic process. The adsorption equilibrium was best described by the Langmuir model, with maximum capacity (Q_m) ranging from 1.63 to 6.25 $\text{mg}\cdot\text{g}^{-1}$ between 298 and 318 K. The Freundlich model also showed a good fit ($R^2 > 0.915$), with $n < 1$, reinforcing the favorability of chemical adsorption [2]. The proposed mechanism (Fig. 2) involves a combined physical-chemical process, with the dominance of chemisorption based on π -complexation between the Fe species of the Pal and the aromatic rings of the sulfur compounds [3].

Conclusions

Palygorskite stood out as a promising adsorbent for diesel desulfurization due to its Fe-rich chemical composition and its textural properties. Adsorption data followed pseudo-

second-order kinetics and the Langmuir model, confirming chemisorption as the determining process. Presenting advantages such as low cost, abundance in nature, and eco-friendly character, it constitutes a viable alternative to the conventional HDS process.

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P04. ADSORPTION BEHAVIOR OF VOLATILE ORGANIC COMPOUNDS ON MOF@HPCM COMPOSITE ADSORBENTS UNDER CONFINED CONDITIONS

Milica Želinská¹, Tomáš Zelenka², Miroslav Almási^{1*}

¹ Department of Inorganic Chemistry, Faculty of Science, Pavol Jozef Safarik University in Kosice, Kosice, Slovakia

² Department of Chemistry, Faculty of Science, University of Ostrava, Ostrava, Czech Republic

* miroslav.almasi@upjs.sk

Volatile organic compounds (VOCs) represent an important class of atmospheric pollutants originating from industrial production, fuel combustion, paints, solvents, household chemicals, and construction materials. Due to their high vapor pressures under ambient conditions, VOCs are readily released into the atmosphere, where they contribute to the formation of tropospheric ozone and secondary organic aerosols while simultaneously posing serious health risks, including respiratory diseases, neurological disorders, and carcinogenic effects. Consequently, the development of efficient adsorbents for vapor-phase VOC removal remains an important environmental challenge. Among currently available approaches, adsorption-based technologies are considered particularly attractive because of their low energy requirements, operational simplicity, and high removal efficiency. In this regard, metal–organic frameworks (MOFs) have emerged as highly promising adsorbents owing to their exceptionally high surface areas, tunable pore architectures, and chemically tailorable adsorption sites. Furthermore, the integration of MOFs with hierarchically porous carbon materials may improve their mechanical stability, accessibility of adsorption sites, and practical applicability.

In this work, two representative MOFs, namely MIL-101(Cr) and UiO-66, together with hierarchically porous carbon monoliths (HPCM) and their corresponding MOF@HPCM composites (see Figure 1), were investigated for vapor-phase adsorption of volatile organic compounds under confined conditions. The prepared materials were characterized using PXRD, nitrogen physisorption at $-196\text{ }^{\circ}\text{C}$, FTIR spectroscopy, and thermogravimetric analysis. Nitrogen adsorption measurements revealed substantial differences in textural properties between the studied materials. MIL-101(Cr) exhibited the highest specific surface area ($S_{\text{BET}} = 3119\text{ m}^2\cdot\text{g}^{-1}$) and mesopore volume ($V_p = 1.91\text{ cm}^3\cdot\text{g}^{-1}$), followed by UiO-66 ($S_{\text{BET}} = 1380\text{ m}^2\cdot\text{g}^{-1}$), while HPCM exhibited a significantly lower surface area of $143\text{ m}^2\cdot\text{g}^{-1}$. The prepared composites contained approximately 38–44 wt.% of the corresponding MOF phase. Although composite formation reduced the overall surface area (e.g. UiO-66@HPCM: $S_{\text{BET}} = 252\text{ m}^2\cdot\text{g}^{-1}$), the hierarchical micro–meso–macroporous structure was preserved.

Adsorption experiments were performed at 25, 35, and 45 °C using twelve VOCs differing in molecular size, polarity, and volatility, including methanol, formaldehyde, benzene, toluene, pyridine, DMF, benzaldehyde, salicylaldehyde, benzyl bromide, dimethyl adipate, aniline, and triethyl phosphate. For most adsorbates, the adsorption profiles showed a continuous increase over time without reaching complete equilibrium within 6 h, whereas highly volatile compounds such as methanol, benzene, and toluene approached saturation more rapidly. Increasing temperature from 25 to 45 °C generally enhanced adsorption capacities due to increased vapor availability in the confined system. The adsorption performance strongly depended on molecular volatility and molecular dimensions, with small low-boiling compounds exhibiting the highest uptakes, while bulky high-boiling VOCs displayed significantly lower adsorption capacities.

Among all investigated materials, MIL-101(Cr) consistently exhibited the highest adsorption capacities for the majority of studied VOCs, whereas UiO-66 showed comparatively lower uptake. Although MOF–carbon composites displayed slightly lower adsorption capacities than pristine MOFs, they provided improved handling properties and potentially higher mechanical stability. The obtained results demonstrate that MOF-based porous materials and MOF–carbon composites represent promising tunable adsorbents for VOC capture and provide a basis for further studies focused on adsorption thermodynamics, recyclability, and long-term stability.

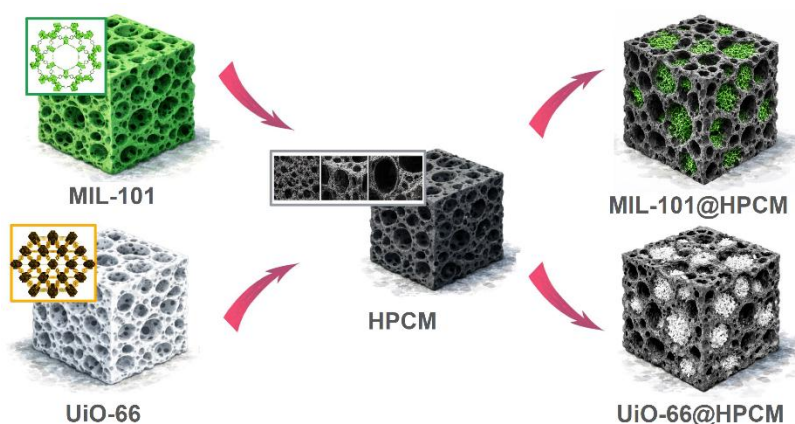


Figure 1 Schematic illustration of pristine MOFs (MIL-101 and UiO-66), hierarchically porous carbon monolith (HPCM), and corresponding MOF@HPCM composite adsorbents prepared for VOC adsorption studies.

Acknowledgment

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P05. Evaluation of MIP-177 MOF for the Adsorption and Sustained Release of NO and H₂S .

**João Pires^{1,*}, Miriam Marques¹, Nélida Almeida², Christian Serre³, Isabel Ribeiro⁴,
Moisés Pinto², Rosana Pinto²**

¹ Centro de Química Estrutural - Institute of Molecular Sciences, Universidade de Lisboa, Portugal.

² CERENA - Instituto Superior Técnico, Universidade de Lisboa, Portugal

³ Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, 75005 Paris, France.

⁴ Research Institute for Medicines (iMed.Ulisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal..

* jpsilva@ciencias.ulisboa.pt

Summary

Exogenous nitric oxide (NO) and hydrogen sulfide (H₂S) show therapeutic promise for cardiovascular diseases, infections, and wound healing. Porous materials like metal-organic frameworks (MOFs) are effective vehicles for gas delivery due to their tunable, biocompatible structures. This study investigates a titanium carboxylate-based MOF called MIP-117 in three forms: as-synthesized, copper-modified, and magnesium-modified. Results were obtained for the adsorption and release of NO and H₂S, including simultaneous liquid-phase release. Initial findings show that the cation type has a mild effect on H₂S adsorption but a much stronger influence on the release profile, likely due to differences in gas affinity. Future work will assess antibacterial effects using single- and dual-gas systems to explore synergistic potential.

Introduction

The controlled administration of exogenous nitric oxide (NO) and hydrogen sulfide (H₂S) has shown therapeutic potential for a range of acute and chronic conditions, including cardiovascular diseases, bacterial infections, and wound healing. In recent years, scientific research has revealed that porous materials, are highly suitable and versatile vehicles for carrying and releasing NO and/or H₂S. Various types of materials were studied such as zeolites [1], clays [2] or metal-organic frameworks (MOFs). The latter are particularly interesting since their tunable composition enables the development of stable and biocompatible frameworks.[3]

In the present work, a titanium carboxylate-based MOF named MIP-117 is explored in three forms: as-synthesized, copper-modified, and magnesium-modified. Results were obtained for the adsorption and release of NO and H₂S, as well as for their simultaneous release in the liquid phase.

Experimental

The adsorption of NO was made using a gravimetric apparatus with a balance (C. I. Electronics, Disbal) suited for vacuum connected to a high vacuum pump system (Pfeiffer Vacuum). The hydrogen sulphide adsorption was made in a volumetric system, equipped with pressure transducers (Balzers Instruments) and a high vacuum pump system. The release of NO and H₂S from the materials were studied by the Griess assay [4] and the DTNB [5] methods, respectively.

Results and Discussion

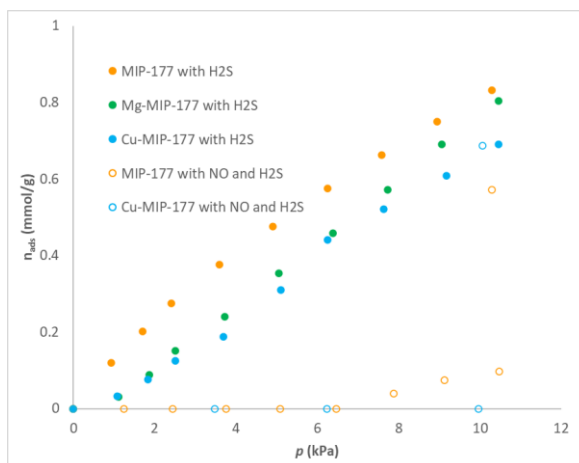


Figure 1- Adsorption isotherms of H₂S at 298 K in the indicated samples, closed points are from samples with H₂S and open points are from samples with preloaded NO before H₂S adsorption.

The adsorption isotherms of H₂S at 298 K (Figure 1) in the initial samples, or in samples previously loaded with NO, indicate only a mild to modest influence of the type of cation on H₂S adsorption. Nevertheless, when the H₂S release profile is also taken into account, the discrepancies become more pronounced, likely reflecting predicted variations in the affinity between the gases and the respective cations. Future work will involve assessing antibacterial activity through both single-gas and dual-gas delivery systems in order to explore possible combined (synergetic) effects

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P06. PEELING AWAY POLLUTION: BIOSORBENTS FROM PINEAPPLE WASTE FOR INDUSTRIAL WATER TREATMENT.

Carolina Agostinho¹, Ana Barroso¹, Inês Moreira², Cidália Botelho², Ricardo Ferreira^{2,*}

¹Department of Chemical and Biological Engineering Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

²LSRE-LCM, ALiCE, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

* rmmferreira@fe.up.pt

Introduction

Agri-food residue valorisation offers a sustainable pathway for developing low-cost materials for wastewater treatment^[1]. In this study, pineapple peel was converted into carbon-based biosorbents through thermochemical processes, including pyrolysis at 600–800 °C under N₂ and N₂+CO₂ atmospheres, combined with calcium and zinc impregnation. The materials were tested in real food and textile wastewaters. Calcium-modified biosorbents activated under N₂+CO₂ exhibited the best performance, achieving a turbidity of 2.4 NTU and colour removal efficiencies up to 92%. In contrast, non-thermally treated samples led to pollutant release due to biomass leaching, highlighting the need for thermal stabilization. Zinc-based materials activated with CO₂ showed reduced efficiency, likely due to structural over-activation and pore collapse. Overall, the results demonstrate that adsorption performance strongly depends on synthesis conditions and confirm the potential of agri-food residues as effective and sustainable adsorbents for complex industrial effluents.

Experimental

Pineapple peel residues were collected, dried, and subjected to chemical extraction prior to incipient wetness impregnation (90 min) with calcium chloride and zinc chloride (10–20 wt.%) to enhance precursor reactivity^[2]. The modified biomass was then thermochemically converted into carbon-based materials via pyrolysis at 600 and 800 °C under a nitrogen atmosphere. A subset of samples was further activated under a combined N₂/CO₂ atmosphere to promote additional porosity development and surface modification.

The adsorption performance of the produced materials was evaluated using two real wastewater matrices: food processing effluent, assessed in terms of turbidity removal, and textile wastewater, evaluated through colour removal at 400 nm. Batch adsorption experiments were conducted under controlled conditions, and removal efficiencies were determined using standard analytical methods.

Results and Discussion

The adsorption performance of the biosorbents varied strongly with preparation method and wastewater type. In food effluent (Figure 1), all materials reduced turbidity compared to untreated water, although some performed worse than raw biomass. The control confirmed that sedimentation and filtration contributed significantly to removal. The best performance was achieved by Ca-impregnated samples activated under N_2+CO_2 , reaching 2.4–2.7 NTU. Raw biomass also showed moderate efficiency, while thermally treated but non-impregnated samples (N-600, N-800, NC-800) performed poorly. Zn-based materials showed inconsistent behaviour, with performance loss under CO_2 activation.

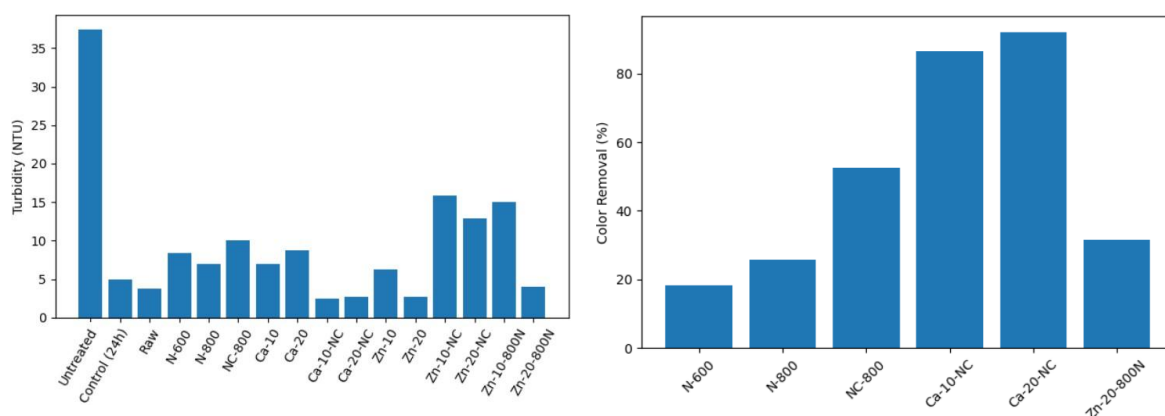


Figure 1. A) Turbidity of food wastewater after treatment with different biosorbents, including untreated and control samples.

In textile effluent (Figure 1B), non-thermally treated samples increased colour due to leaching, confirming the need for thermal stabilization. Pyrolyzed materials achieved moderate removal (18–26%), improved by CO_2 activation (~52%). The highest efficiency (up to 92%) was obtained with Ca-modified, activated samples. Zn-based materials under N_2+CO_2 showed low performance due to structural degradation.

Overall, the results highlight that adsorption performance is highly dependent on both the synthesis route and the characteristics of the target effluent. The combination of calcium impregnation and controlled thermochemical activation emerges as the most effective strategy, while excessive activation conditions can be detrimental to material performance.

Acknowledgments

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P07. Metal Organic-Framework production process with ligand recovery: process optimization, life cycle, and production cost assessments.

Beatriz Cassuriaga¹, Andreia Santos¹, Tarik Aaboub², Vanessa Pimenta², Farid Nouar², Christian Serre², Ana Carvalho¹, Moisés L. Pinto^{3*}

¹ CEGIST, Centro de Estudos de Gestão do Instituto Superior Técnico, Universidade de Lisboa.

² Institut des Matériaux Poreux de Paris (IMAP), ESPCI Paris, École Normale Supérieure de Paris, CNRS, PSL University.

³ CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa.

* moises.pinto@tecnico.ulisboa.pt

Abstract

Metal organic-frameworks (MOFs) are hybrid porous materials with tuneable pore sizes and chemistry, which are being considered for many applications. Yet, several of applications require the use of a significant amount of adsorbent and thus the production of MOFs needs to be scaled up if they are to be used in large scales. After a production protocol is developed using green synthesis conditions, a suitable industrial process needs to be established. In this study, we focus on the production process optimization for a topical MOF, MIL-100(Fe), considering process intensification and ligand recovery, which is a main source of the MOF production cost. Since this recovery implies the investment on additional equipment, the use of more raw materials and energy, we assess the impact of these optimizations on the life cycle assessment, and production cost of the MIL-100(Fe).

Introduction

Within the framework of the European project SIMIACCI, we are exploring the application of metal-organic frameworks to contribute to the preservation of collections in galleries, libraries, archives and museums that require strict control of indoor air quality to limit degradation caused by atmospheric contaminants. The aim is to achieve a better control of pollutants with less energy consumption, by improving the conventional ventilation and filtration systems that have limited or no removal capabilities. We are focusing on the application of advanced adsorbent materials, MOFs, which have demonstrated enhanced capabilities for the removal of several VOCs in the presence of air moisture.[1-3] One very efficient material is MIL-100(Fe), an iron(III) tricarboxylate MOF built up from trimers of iron octahedra, linked by the benzene-1,3,5-tricarboxylate (BTC) ligand. To be applied in the future as adsorbents for indoor air quality improvement, the production of this material needs to be scaled to multikilogram or tonne. Recently, we estimated the production costs for MIL-100(Fe)

considering two production routes and found that the costs were mostly dependent on the ligand cost [4]. In the present work, we focus on the possible recovery of the ligand BTC to be recycled for reuse in the production and assess the possible implications on the production cost and life cycle assessment.

Methods

Based on a previous process proposal using iron sulphate as the metal source [4], we developed a solvent extraction process to recover the BTC from the stream obtained after filtration, using the process simulator ASPEN plus. The process was optimized to maximize the recovery and minimize the solvent loss and energy consumption. To quantify the environmental impacts associated with the industrial production of MIL-100(Fe) through a cradle-to-gate Life Cycle Assessment (LCA), the production process of the MOF with and without the ligand recovery was considered. The models were implemented in SimaPro using Ecoinvent database, considering a functional unit of 1 kton of material. This assessment identifies the main contributors within the production process and evaluates environmental performance, supporting the development of more sustainable solutions.

Results and Discussion

Based on our process simulations, the application of common solvent extraction strategies can be successfully applied to achieve high BTC recoveries (~98%), with only ~1 ton BTC loss for 1kton MOF production. Yet, this BTC recovery comes with a significant energy expense to purify and reuse the extraction solvent. Considering this energy cost increase and the savings due to the recovered BTC, we estimated a net saving of ~1M\$/year in the operational costs for an estimated price of 20\$/kg for the BTC, which indicates an interesting economic benefit for the recovery option. By applying a sensitive analysis to the ligand price, we observed that the recovery is not economically interesting for values below 3.5\$/kg. Process simulations indicate that the increase in energy consumption will be a critical point to be evaluated in the LCA of BTC recovery, in order to assess its viability in environmental terms. Further assessment is ongoing to consider the process optimization for heat integration, the LCA for the new optimized systems and effect on the plant investment cost.

Acknowledgments

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P08. Tailoring CO₂ adsorption in MOF derived carbons through precursor chemical modification.

M. Karla López González^{1*}, Javier Narciso¹

¹ *University Institute of Materials (IUMA), Inorganic Chemistry Department, University of Alicante, Alicante (Spain).*

* *mariakarla.lopez@ua.es*

Summary

CO₂ capture through adsorption has attracted increasing interest as a potential strategy to mitigate greenhouse gas emissions. In this context, MOF-derived carbons constitute promising materials due to their ability to retain part of the precursor microporosity while promoting a homogeneous incorporation of heteroatoms into the carbon matrix after pyrolysis. In this work, nitrogen, sulfur, and copper doped carbons were synthesized from ZIF-8 post-synthetically modified with N and S rich ligands and copper acetate, followed by pyrolysis at 750 and 900 °C. The obtained materials were characterized by PXRD, N₂ and CO₂ adsorption isotherms, SEM, TGA-MS, FTIR, Raman spectroscopy, and XPS. The results showed that the chemical nature of the precursor significantly influences pore development and low-pressure CO₂ adsorption, achieving values up to 113.74 cm³ g⁻¹ at 273 K and P/P₀ ≈ 0.03.

Results

The textural properties of the carbons obtained after pyrolysis at 900 °C are summarized in Table 1. While the C1 series preserved the highly microporous character of the parent ZIF-8-derived carbon, the C2 series experienced a substantial deterioration of its textural properties, reflected by marked decreases in both surface area and micropore volume. The most modified samples displayed reductions approaching 60% relative to the reference material, highlighting the strong impact of precursor chemistry on the evolution of porosity during pyrolysis.

Table 1- Surface area and pore structure characteristics of the carbons obtained by pyrolysis of modified ZIF-8 precursors at 900 °C

Carbons	Area (m ² /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{total} (cm ³ /g)
C.ZIF-8.900	865	0.32	0.17	0.49
C1.1-0.2.900	890	0.33	0.17	0.50
C1.1-0.5.900	919	0.34	0.18	0.52
C1.1-1.900	752	0.28	0.18	0.50
C2.1-0.2.900	636	0,24	0,39	0.63
C2.1-0.5.900	317	0,13	0,27	0,4

The CO₂ adsorption isotherms recorded at 273 K for the carbons pyrolyzed at 900 °C are presented in Figure 1. Marked differences in adsorption performance were observed among the studied materials, with C1.1-0.5 exhibiting the highest uptake, reaching 113.7 cm³ g⁻¹ at P/P₀ ≈ 0.03. In general, materials displaying larger micropore volumes achieved higher CO₂ adsorption capacities, whereas the progressive loss of microporosity observed in the C2 series resulted in a substantial decline in adsorption performance. These findings point to a close relationship between the microporous structure developed during carbonization and low-pressure CO₂ uptake.

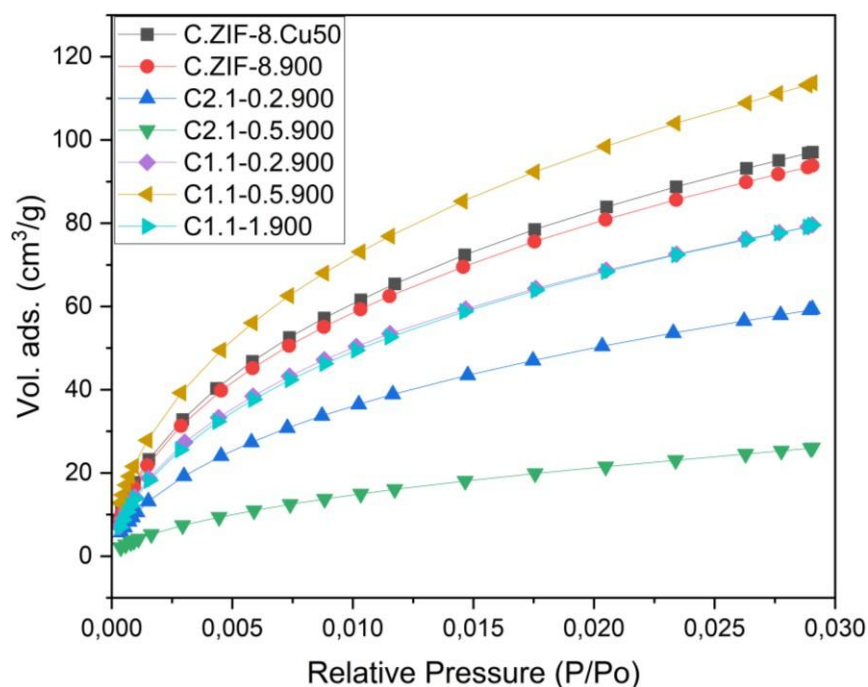


Figure 1- CO₂ adsorption isotherms at 273 K for carbons pyrolyzed at 900 °C

The results demonstrate that chemical modification of the ZIF-8 precursor constitutes an effective strategy for tailoring the textural properties of MOF-derived carbons and, consequently, their CO₂ adsorption behavior. In particular, the C1 series enabled the preservation and enhancement of microporous characteristics relative to the parent material, leading to the highest adsorption capacities, whereas more extensive structural alterations resulted in a progressive deterioration of both microporosity and CO₂ uptake.

P09. Biogas upgrading using sustainable activated carbons obtained from sewage sludge.

Daniel Moya, Carol Khayat, Daniel Gómez, Rubén Calero, V. Ismael Águeda, José Antonio Delgado

Catalysis and Separation Processes Group (CyPS), Chemical and Materials Engineering Department, Universidad Complutense de Madrid, 28040 Madrid, Spain;

**viam@ucm.es*

Introduction

In Europe, biogas production reached 22 bcm in 2023, accounting for 7% of natural gas consumption, with projections of up to 111 bcm by 2040. Biogas, composed mainly of methane and CO₂ (40–60%). High purity biomethane is mainly produced from raw biogas through an upgrading process in which carbon dioxide and other contaminants are removed [1]. Moreover, is a renewable source of biogenic CO₂, an essential feedstock for the production of synthetic fuels. Cyclic adsorption-desorption processes (vacuum swing adsorption, VSA) have already proven for biogas upgrading [2-3]. Several carbon based adsorbents such as, carbon molecular sieves (CMS), and activated carbons have been extensively used for this application [4]. The industry is looking for new sustainable precursors such as biomass, sewage sludge and others to obtain selective adsorbents and to increase the circularity of waste products. In this work, the synthesis of activated carbons as adsorbents from sewage sludge has been studied. The biogas upgrading to biomethane has been analysed with the best samples obtained.

Experimental

Dried sewage sludge has been obtained from Valoriza. Activated carbons have been synthesised by means of pyrolysis followed by acidic washing. Different temperatures (450°C, 650°C and 850°C) have been tested using a nitrogen flowrate of 30 mL/min. The materials obtained have been washed with HCl solutions (0,5M-5M) with different solution to solid ratios (50 and 25) for 24 hours at 25°C. The adsorbents were washed until neutral pH and dried at 100°C. The final materials were characterized using TG, N₂ adsorption-desorption isotherms at 77K, and helium pycnometry. Adsorption equilibrium isotherms of CO₂ and CH₄ were measured using a BELSORP MAX II volumetric equipment. Breakthrough curves were measured and the kinetic parameters were obtained using a mathematical model. A Vacuum Swing Adsorption process was simulated using PSASIM® [5].

Results and Discussion

Table 1 presents the synthesis conditions and the characterization results obtained. As the pyrolysis temperature increased, the ash content increased due to the organic matter condensation and conversion. After the acid treatment, all the samples enhanced their textural properties. The pore volume and specific surface areas increased as the HCl concentration and the solution to solid ratio increased. Three different samples were selected D6A1, D3A1 and D7A3.

Table 1- Samples obtained and characterization results.

SAMPLE	Temperature	Solution/Solid	HCl	Pore volume	Surface Area	ASH
	(°C)		(Molarity)	(cm ³ ·g ⁻¹)	(m ² ·g ⁻¹)	(%)
D3_A1_100	650	50	3	0,274	178,2	
D7_A1_50	650	25	5	0,226	160,3	43,8
D4_A2_50	650	25	3	0,248	151,3	
D3_A2_50	650	25	3	0,239	149,9	45,1
D7_A5_50	650	25	1	0,233	146,1	47,0
D6_A1_100	850	50	3	0,232	127,8	
D7_A3_50	650	25	0,5	0,177	127,8	48,5
D6_A2_50	850	25	3	0,214	122,3	58,1
D5_A1_100	450	50	3	0,058	25,6	
D5_A2_50	450	25	3	0,053	11,0	38,8

Figure 1 presents the adsorption isotherms at 25°C of N₂ and CO₂ onto the selected adsorbents. As can be seen in the figure, all the adsorbents showed a high selectivity to CO₂. The kinetic parameters have been obtained and the VSA cycle has been simulated. Very low differences have been obtained in the parameters.

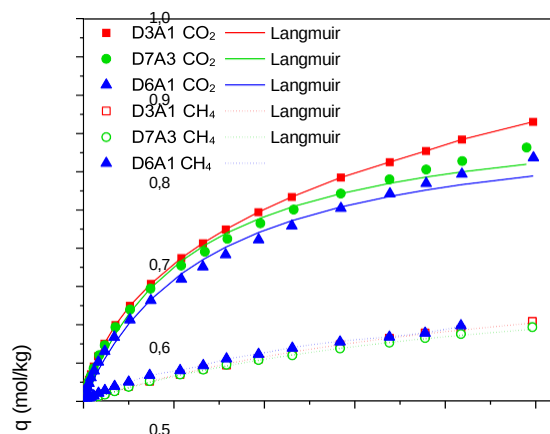


Figure 1- Isotherms of adsorption at 25C.

Acknowledgments

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P10. Uranium and critical elements remotion from phosphogypsum leachates – an insight of adsorption mechanism onto clay minerals.

Aníbal López-Marín^{1,2*}, Rafael León Cortegano³, Rosa Martín-Rodríguez^{1,2}, Ana C. Perdigón^{1,2}, Carlos Ruiz Cánovas³

¹*Departamento de Química e Ingeniería de Procesos y Recursos (QUIPRE), Universidad de Cantabria, Av. de los Castros 46, 39005, Santander, Spain.*

²*Nanomedicine Group, Instituto de Investigación Marqués de Valdecilla (IDIVAL), Av. Cardenal Herrera Oria s/n, 39011, Santander, Spain.*

³*Departamento de Ciencias de la Tierra, Universidad de Huelva, Av. del Tres de Marzo s/n, 21071, Huelva, Spain.*

* anibal.lopez@unican.es

Phosphogypsum leachates contain significant concentrations of radionuclides and critical elements, including uranium and rare earth elements (REE). This study evaluates the adsorption mechanisms of these elements using di- and trioctahedral clays under acidic conditions. Batch experiments with montmorillonite, saponite, Laponite, and Nan-micas were conducted at different pH values and contact times. Montmorillonite showed high structural stability and promoted REE–phosphate co-precipitation, especially for light REE. Synthetic trioctahedral clays exhibited structural damage below pH 4.5 but achieved nearly complete uranium removal. The results highlight clay minerals as promising materials for phosphogypsum leachate decontamination.

Introduction

Phosphogypsum is a byproduct of phosphoric acid (H_3PO_4) production, an essential raw material for the industrialized production of fertilizers. The generation of phosphogypsum as a byproduct has led to significant environmental problems, since impurities present in phosphate rock are retained in the porous structure of the phosphogypsum, leaving fractions of sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) ions acting as acidifying agents [1]. These impurities are found in high concentrations in the phosphoric residue, characterized by a significant content of heavy metals, metalloids, and radionuclides [2].

Interestingly, authors have confirmed the presence of rare earth elements (REEs) in significant concentrations in phosphogypsum leachates [3,4]. The following study describes the treatment conditions for REE and uranium remotion from phosphogypsum leachates (PGL) with several clay minerals, in the province of Huelva. The critical elements removal treatment includes the use of di- and trioctahedral smectite clays in

contact with the PGL, allowing the adsorption of these elements on the surface and its interlayer space.

Experimental Methodology

For the study of the adsorption of uranium and rare earth elements from phosphogypsum leachate, each clay sample (Montmorillonite SWy-2, Saponite Sumecton SA, Laponite RD and Na-*n*-micas) was placed in contact in a ratio of 100 mg of clay per 30 mL of PGL in a rotary shaker. The adsorption process was measured at different initial pH values (2.1, 3.0, 4.5 and 6.0), previously neutralized with 0.1 M NaOH solution to prevent degradation of the clay structure under acidic conditions. The contact time of the PGL–clay systems in batch mode was set at a maximum of 24 h, with 20 mL aliquots taken at times $t = 0.5, 1, 2, 4, 6$, and 24 h.

After each batch, each suspension was centrifuged, separating the solid and drying at 50°C. The powder solid was subsequently studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). REE concentration were measured in the supernatant by optical emission spectroscopy (ICP-OES).

Results

Efficient adsorption of REE was achieved through the interaction between phosphogypsum leachates and the dioctahedral clay montmorillonite within the pH₀ range of 2.1–3.0. Adsorption occurred through the apparent surface precipitation of REE phosphates, with a predominance of light REE such as La, Ce, and Nd. Therefore, it was established that the greater structural stability of the 2:1 montmorillonite layers, into moderately acidic pH conditions and the high concentration of PO₄³⁻ ions in the leachates, favors the surface adsorption of REE onto dioctahedral clay through phosphate co-precipitation.

Meanwhile, the studied clays exhibited different structural behaviors depending on their di- or trioctahedral nature under the acidic conditions of the PGL and as a function of contact time, resulting in lower structural damage in the dioctahedral smectite montmorillonite compared to the synthetic trioctahedral clays saponite and Laponite. A significant and rapid increase of pH solution of the synthetic clays was identified at initial pH values below 4.5, promoting the formation of new sodium- and calcium-bearing phases such as halite and fluorite. Nevertheless, the studied trioctahedral clays demonstrated a total removal mechanism of uranium at acidic conditions below pH 3.0.

Conclusions

Recovery of REE from phosphogypsum leachates was strongly influenced by the clay mineral phases present in the PGL systems. Montmorillonite preserved its structure under acidic conditions (pH 2.1–3.0), promoting REE–phosphate co-precipitation onto

the clay surface. Halite formation was observed in montmorillonite, saponite, and Na-*n*-mica systems, whereas fluorite was formed in the presence of Laponite. At pH values below 3.0, synthetic clays such as saponite and Laponite achieved nearly complete removal of REE and U, up to 180 µg/L of uranium. REE removal capacity remained low significant for practical scale-up processing (<3.5 µg/L). However, uranium mechanism retention with clay minerals results as promising alternatives por decontamination of PGL.

Acknowledgments

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P11. CO₂ recovery by using a three-bed PSA cycle with BPL activated carbon.

Daniel Gómez^{1*}, Carol Khayat¹, Vicente Ismael Agueda¹, José Antonio Delgado¹

¹ *Catalysis and Separation Processes Group (CyPS), Chemical and Materials Engineering Department,*

Universidad Complutense de Madrid, 28040 Madrid, Spain;

** dangom25@ucm.es*

The main objective of this work is to optimize the operating conditions of a PSA cycle to maximize CO₂ purity and recovery in the capture of CO₂ from flue gas. The PSA cycle proposed uses three beds [1]. The kinetic parameters and the use of BPL-activated carbon were determined by previous work. To maximize the purity and recovery of the CO₂, simulations were performed varying the time of the cycles and the velocities of the feed and the rinse. The feed gas composition used in the simulations was 17% CO₂, 79% N₂, and 4% O₂ [1]. The high and low pressures used in this cycle were 1.5 and 0.1 bar [1].

Introduction:

Carbon dioxide (CO₂) capture has become a key strategy in reducing gas emissions and mitigating climate change. Among the available technologies, Pressure Swing Adsorption (PSA) stands out due to its low energy requirements and high separation efficiency. In this work, a three-bed PSA cycle using BPL activated carbon was studied through simulations to evaluate the influence of operating conditions on CO₂ purity and recovery from a gas mixture representative of post-combustion streams.

Experimental & results:

The cycle, with its steps, is shown in Figure 1, and the order of the steps each bed is put through is shown in Table 1.

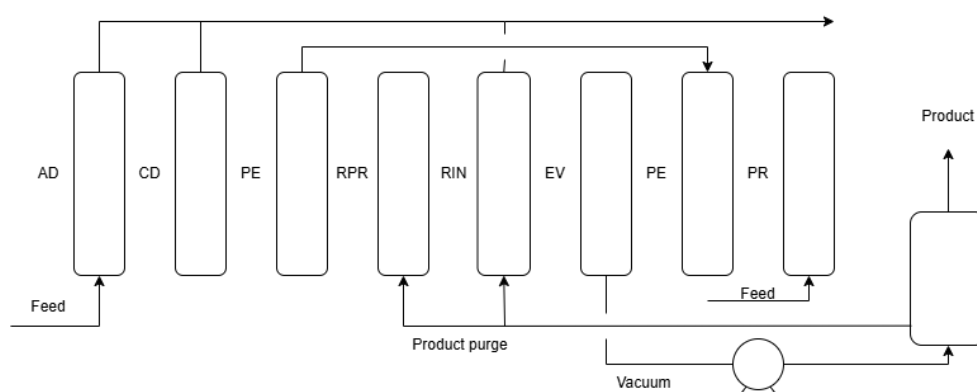


Figure 1- Scheme of the PSA cycle.

Table 1- Order of the steps the beds are put through.

BED 1	AD S	CD	DE Q	RP R	RIN		ID	EV		PE Q	PR		
BED 2	EV		PE Q	PR	ADS	CD	DE Q	RPR	RIN		ID	EV	
BED 3	RIN		ID	EV			PE Q	PR	ADS	CD	DE Q	RP R	RIN

(ADS=Adsorption, PR=pressurization, CD=cocurrent despressurization, PEQ=pressure equalization, DEQ=despressurization equalization, EV=evacuation, RIN=rinse, RPR=repressurization and ID=idle)

Different simulations were made to search for the optimal working conditions of the PSA cycle, to observe how they affect the purity and recovery obtained. In Table 2, the working conditions studied are shown along with the CO₂ productivity, purity, and recovery in the heavy product.

Table 2-Simulation results.

Nº sim	tcycle (s)	ufeed (m/s)	urinse (m/s)	CO ₂ productivity in heavy product		Purity and recovery in heavy product	
				(molCO ₂ /(kg ads*s))	(molCO ₂ /(m ³ bed*s))	CO ₂ (%)	CO ₂ (%)
1	40	0.3	0.1	2.870E-04	1.604E-01	89.901	44.0189
2	48	0.25	0.08	2.452E-04	1.372E-01	89.808	45.1596
3	32	0.375	0.125	3.687E-04	2.060E-01	88.195	45.3220
4	33.33	0.3	0.1	4.018E-04	2.250E-01	82.373	58.0500
5	26.664	0.375	0.125	5.096E-04	2.850E-01	80.338	58.9480
6	39.996	0.25	0.83	3.307E-04	1.850E-01	83.782	57.3680
7	46.7	0.3	0.1	1.810E-04	1.010E-01	95.499	29.1330
8	44	0.32	0.106	1.938E-04	1.080E-01	95.212	29.2820
9	50	0.28	0.093	1.692E-04	9.469E-02	95.872	29.1730
10	53.333	0.3	0.1	1.061E-04	5.941E-02	98.446	17.6580
11	42.6664	0.375	0.125	1.657E-04	8.772E-02	99.923	20.8800

As we can see in Table 2, the lower the time cycle the higher the productivity and CO₂ recovery obtained, on the contrary, the higher the time cycle higher purity percentages of CO₂ obtained in the heavy product. These results indicate that the longer the PSA cycle operates high purity heavy product is obtained but as a sacrifice the recovery is lower. Cycle time showed the strongest influence on process performance, with shorter cycles favoring CO₂ recovery and productivity, while longer cycles increased CO₂ purity.

Conclusions:

The result obtained from the simulations forces us to choose between high purity or high recovery and productivity. The maximum CO₂ purity obtained was close to 100%, although associated with relatively low recoveries. These results suggest that a single PSA cycle is insufficient to simultaneously maximize purity and recovery, making multistage or multicycle PSA configurations a promising alternative for future work.

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P12. Biogas purification via PSA using carbon molecular sieve CMS-3K simulation study.

Carol Khayat, Daniel Gomez, Vicente Ismael Agueda, Jose Antonio Delgado

¹ *Catalysis and Separation Processes Group (CyPS), Chemical and Materials Engineering Department, Universidad Complutense de Madrid, 28040 Madrid, Spain;*

** carolkha@ucm.es*

Summary

This study evaluates a dual-bed PSA system for biogas purification using experimental kinetic and equilibrium data. Simulations in PSASIM optimize the relationship between adsorption time and feed velocity to meet regulatory purity standards. Results identify optimal conditions that maximize methane recovery while minimizing energy consumption, providing a framework for efficient process design.

Introduction

This work focuses on purifying biogas to meet environmental standards for CH₄, CO₂, O₂, and N₂. Adsorption isotherms and kinetic parameters were experimentally determined using a CMS-3K bed under controlled conditions. These parameters were integrated into PSASIM software to simulate PSA cycles, optimizing the relationship between cycle time and velocity. The study evaluates performance indicators including purity, energy consumption, and productivity to define operational limits for biogas upgrading.

Experimental

Isotherms of adsorption , breakthrough curves and kinetic parameters:

Adsorption isotherms were measured for all gases on CMS-3K. Additionally, kinetic parameters were experimentally determined using an adsorption bed packed with CMS-3K. Breakthrough curves were recorded for carbon dioxide, methane, oxygen, and nitrogen across five different flow rates and three temperatures (25, 40, and 65°C). The resulting data were modelled using PSASIM software to calculate kinetic coefficients (s⁻¹) and activation energies (J/mol).

PSA Description

A dual-bed Pressure Swing Adsorption (PSA) cycle was simulated based on literature configurations for biogas upgrading. Each bed follows a sequence of five primary steps: 1) adsorption, 2) depressurization, 3) evacuation,

4) pressure equalization, and 5) pressurization [1].

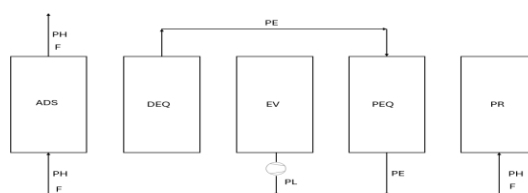


Figure 1- PSA adsorption cycle

Simulation and Optimization

The PSA process was modelled in PSASIM using a 1 m bed length with operating pressures ranging from 0.1 bar (low) to 1.5 bar (high). The primary objective was to meet the BOE-A-2018-14557 Spanish purity standards: Methane: 90 mol % lower limit; Carbon dioxide: 2 mol % upper limit; Oxygen: 1 mol % upper limit. Optimization focused on the relationship between adsorption time (t_{ads}) and feed velocity (u_f), defined by the feed gas to bed volume ratio (FGBVR)= adsorption time* feed velocity/bed length.

Results

Multiple simulations were conducted using different adsorption time-to-feed velocity ratios to meet required purity standards. Table 1 summarizes the results for methane purification under various operational parameters that achieved the legally required purity levels for CH₄, CO₂, and O₂.

Table 1- PSA results

FGBVR	t_{ads} (s)	t_{ciclo} (s)	u_f (m/s)	Energy (kJ/mol CH ₄)	Purity (Light) %CH ₄	Purity (Heavy) %CH ₄	Recovery %CH ₄	Productivity CH ₄	
								molCH ₄ /(kg ads*s)	molCH ₄ /(m ³ bed*s)
2	100	150	0.020	10.79	97.18	19.00	83.07	3.49E-04	2.37E-01
1.4	60	90	0.023	12.19	97.65	23.87	77.32	4.06E-04	2.75E-01
1.4	80	120	0.018	12.21	98.20	24.09	76.77	3.04E-04	2.06E-01
1.4	100	150	0.014	15.28	99.06	31.75	65.42	2.38E-04	1.61E-01

From these results, it is observed that at a ratio of 2, the cycle time (t_{ciclo}) was higher (150 s) compared to the initial simulations at 1.4. This configuration yielded the highest recovery (83.07%) and the lowest energy consumption (10.79 kJ/mol CH₄). Conversely, reducing velocity at a fixed relation increases purity but negatively impacts productivity.

Conclusion

The integration of experimentally determined kinetic parameters into a dual-bed PSA simulation successfully identified optimal operating windows for biogas upgrading. The study demonstrates that achieving high methane purity (above 97%) is feasible under low-pressure conditions (0.1 to 1.5 bar) while meeting BOE-A-2018-14557 standards. The ratio between adsorption time and feed velocity proved to be a critical design factor; a higher ratio favors recovery and energy efficiency, whereas lower velocities enhance gas purity at the expense of productivity. These findings provide a robust framework for the design and optimization of small-scale biogas purification units.

Acknowledgments

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P13. MERCURY ADSORPTION BY SULFUR MODIFIED COKE DEPOSITS FROM BIO-OIL CATALYTIC STEAM REFORMING.

Óscar R. Montoro¹, Pedro Megía¹, María José López-Muñoz^{2,3}, Alicia Carrero^{1,3}, Amaya Arencibia¹

¹ Dpto. Tecnol. Química, Energética y Mecánica, Univ. Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Spain.

² Dpto. Tecnol. Química y Ambiental, Universidad Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Spain.

³ Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS), URJC, C/Tulipán s/n, 28933 Móstoles.

* e-mail: amaya.arencibia@urjc.es

Bio-oil steam reforming is a promising route for renewable hydrogen production, although it generates coke deposits as catalyst deactivating by-product. In this work, these coke residues were valorized through its functionalization with cysteamine to produce adsorbents of Hg(II) from aqueous media. Adsorption isotherms showed a significant improvement in mercury removal after functionalization. Overall, the results highlight a sustainable strategy to reuse coke deposits into effective adsorbents for water treatment.

Introduction

Bio-oil steam reforming is considered a promising route for renewable hydrogen production, contributing to the decarbonization of the energy system through the valorization of biomass-derived feedstocks. The viability of this process is related to the development of suitable catalysts capable of producing H₂-rich gas streams, despite the presence of secondary reactions that also lead to coke formation. Coke deposits have been considered as a catalyst deactivating by-product; however, they can be valorized, avoiding energy-intensive regeneration steps, using a novel and sustainable strategy as an alternative to conventional adsorbents for several applications including water treatment. On this basis, this work proposes the functionalization of coke deposits to enable their use as adsorbents for toxic contaminants such as Hg(II) in aqueous media.

Experimental

Co/SBA-15 catalyst was prepared to get 7 wt.% of cobalt loading. Bio-oil steam reforming was carried out at 600°C and 30.2 h⁻¹ of WHSV using a fixed-bed reactor fed with an aqueous mixture of bio-oil model compounds containing 1.57, 8.25, and 17.5 mol% of phenol, hydroxyacetone and acetic acid, respectively [1]. After 50 h, the coke-deposited catalyst was recovered and then oxidized using mixtures of HNO₃, H₂SO₄,

and H_2O_2 under reflux. The solid was filtered, thoroughly washed, and dried overnight at 110°C . After oxidation, the coke material was subsequently functionalized with cysteamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-SH}$) via EDC/NHS (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N-hydroxysuccinimide) [2]. Materials were characterized by N_2 physisorption, TGA, elemental analysis, TEM, ATR-FTIR and Raman spectroscopy. Mercury batch adsorption experiments were performed by contacting functionalized coke with aqueous HgCl_2 solutions at 20°C , modifying the initial concentration ($1\text{-}200\text{ mg}\cdot\text{dm}^{-3}$). Aqueous mercury concentration was determined by cold vapor atomic fluorescence spectroscopy (CV-AFS) following the EN 13506 standard.

Results and Discussion

As a result of bio-oil steam reforming, a hydrogen-rich gas outlet stream (54 mol%) was obtained. The recovered coke-deposited catalyst displayed a specific surface area of $183\text{ m}^2\cdot\text{g}^{-1}$ and a pore volume of

$0.3\text{ cm}^3\cdot\text{g}^{-1}$. The coke percentage determined by TGA was 49.5 wt.%. Figure 1 shows TEM images of coke deposited catalyst that contains SBA-15 mesoporous structure combined with deposited coke nanotubes.

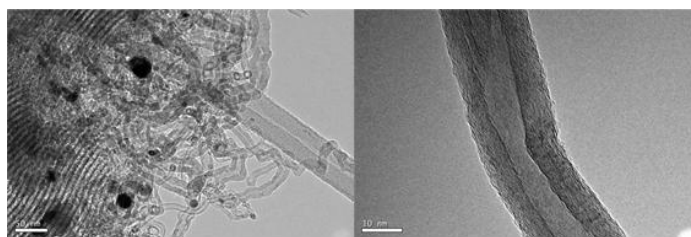


Figure 1. TEM micrographs of coke deposited catalyst after 50 h in bio-oil model compounds steam reforming.

Coke-deposited catalyst was successfully functionalized with cysteamine. After the first oxidation step, vibrational spectroscopy showed that the oxygenated surface groups have been introduced onto the surface of coke deposits by acid treatment. The incorporation of cysteamine yielded coke-deposited material functionalized with amino and sulfur groups [2], with a significant amount of organic content (up to 2.7 and 4.7 wt% of nitrogen and sulfur, respectively). Mercury removal by both coke-deposited catalyst and cysteamine-functionalized coke, was evaluated through their equilibrium isotherms (Figure 2), which were well described by the Langmuir model. As it can be seen, a significant enhancement of Hg(II) adsorption after functionalization was produced due to the incorporation of thiol ($-\text{SH}$) groups with maximum values of

164.0 mg·g⁻¹ for the functionalized material compared to 63.3 mg·g⁻¹ for the coke-deposited catalyst.

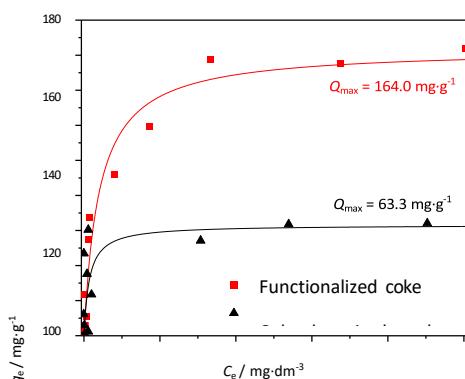


Figure 2. Aqueous Hg(II) adsorption isotherms on coke-deposited and cysteamine-functionalized coke materials.

Conclusions

The cysteamine-functionalization of coke deposits enables the production of effective adsorbents for aqueous Hg(II), thereby valorizing coke residues through a sustainable strategy.

Acknowledgments

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P14. Efecto del método de aglomeración de CALF-20 en la captura de CO₂ de gases de combustión mediante PSA.

Luis Enriquez^{1*}, Alvaro Trujillo^{1,2}, Ernesto Simón², María Martín¹, Ismael Águeda¹, José Antonio Delgado¹

¹ Grupo de Catálisis y Procesos de Separación. Departamento de Ingeniería Química. Universidad Complutense de Madrid. Avda. Complutense, 28040 Madrid, España.

² Técnicas Reunidas Internacional. Av. Burgos 89, Edificio Adequa 5, 3a planta. 28050, Madrid, Spain

* lenrique@ucm.es

El trabajo muestra el efecto del método de aglomeración del CALF-20 en la captura de CO₂. Para ello se sintetizó el MOF CALF-20 y se caracterizó mediante DRX y TG. Posteriormente, se aglomeró y se obtuvieron las isothermas de adsorción y las curvas de rotura de CO₂ y N₂ con cada muestra a distintas temperaturas y caudales. A partir del ajuste a un modelo matemático de los datos experimentales, se obtuvieron los parámetros de equilibrio y cinéticos con los cuales fue posible simular ciclos PSA, obteniéndose purzas de CO₂ superiores al 95 % y porcentajes de recuperación mayores al 90 %.

Introducción

El informe de la AIE correspondiente al año 2018 destaca la creciente demanda mundial de energía. Este incremento se relaciona directamente con el consumo de combustibles utilizados para satisfacer dicha demanda en constante crecimiento. En consecuencia, las emisiones totales de gases de efecto invernadero también se han incrementado considerablemente, principalmente las de CO₂. [2]

Los metal-organic frameworks (MOF) y los polímeros de coordinación se han investigado recientemente para una amplia gama de aplicaciones relacionadas con el almacenamiento de gases de interés energético, como el hidrógeno y el metano. Además de reducir las emisiones de CO₂, los MOF pueden adsorber directamente cantidades significativas de este gas. [3]. El MOF CALF-20 es un adsorbente prometedor para de captura y almacenamiento de carbono (CCS).[4]

Procedimiento Experimental

El MOF CALF-20 se sintetizó siguiendo el procedimiento descrito por Jared et al. [1]. Se realizaron dos tipos de aglomeraciones, una mediante prensado del sólido (muestras 3T y 5T) y otra usando carboximetilcelulosa como aglomerante, seguida de extrusión (muestra N3). Las isothermas de equilibrio de adsorción de CO₂ y N₂ se obtuvieron a 298 K, 313 K y 338 K mediante un equipo volumétrico BELSORP MAX II para cada uno de los

MOF modificados y para el CALF-20 en polvo. Los datos experimentales de equilibrio se ajustaron al modelo de doble Langmuir. Las curvas de rotura se midieron en un lecho fijo montado en el horno de un cromatógrafo Varian CP-3800 y acoplado a un detector TCD. Los experimentos se realizaron a 298 K, 313 K y 338 K y a distintas fracciones molares de adsorbato, para cada uno de los MOF obtenidos. La simulación de los ciclos PSA se realizó con el programa PSASIM elaborado por el profesor José Antonio Delgado.

Resultados y Discusión

Los resultados del DRX mostraron que el MOF CALF-20 se sintetizó correctamente. La tabla 1 resume los parámetros cinéticos obtenidos del proceso de adsorción de CO₂ para cada una de las muestras. Se puede observar que el MOF modificado 5T presenta una mayor resistencia a la transferencia de masa seguido del 3T y del N3. La figura 1 muestra las curvas de rotura experimentales y las ajustadas por el modelo, a partir de los cuales se obtuvieron los parámetros cinéticos mostrados en la tabla 1.

Tabla 1. Parámetros cinéticos.

Adsorbente	CO ₂			N ₂		
	K _{so} (s ⁻¹)	E _a (J/mol)	K _s (s ⁻¹)	K _{so} (s ⁻¹)	E _a (J/mol)	K _s (s ⁻¹)
N3	0.87507036	6519.97865	0.0631	82.7775912	12347.7815	0.5683
3T	2.95408891	11479.8031	0.0288	83.4624198	11621.4327	0.7681
5T	9.97938204	15535.2247	0.0189	4.69324965	4309.90796	0.8248

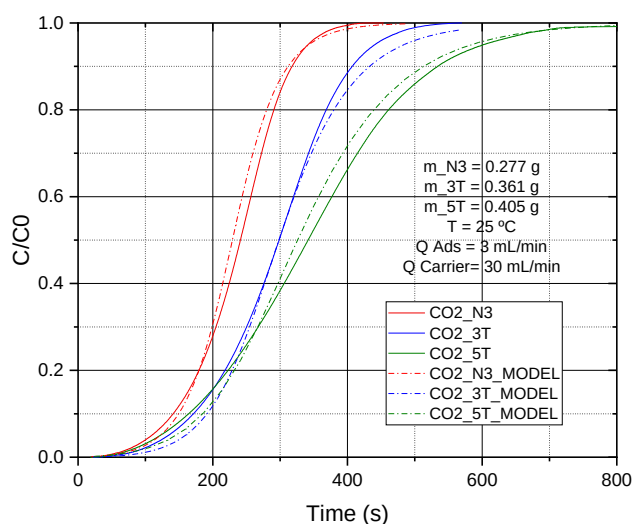


Figura 1. Curvas de rotura de adsorción de CO₂ a 298 K de los diferentes adsorbentes.

Conclusiones

El CALF-20 muestra una gran capacidad y selectividad para la adsorción de CO₂ que no se ve disminuida significativamente con la aglomeración. Además, la simulación de los ciclos PSA muestra purezas de CO₂ superiores al 95 % y porcentajes de recuperación mayores al 90 %. Estos resultados son comparables con los obtenidos con otros que se obtienen con otros procesos con la ventaja de un menor consumo energético.

Agradecimientos

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P15. Innovative electrospun geopolymer/zeolite/PVA composite membranes for CO₂ capture and gas separation.

Mariana Schneider^{1,2}, Mar Calzado-Delgado³, Enrique Rodríguez-Castellón², M. Olga Guerrero-Pérez³, Dachamir Hotza¹, Agenor DeNoni Junior¹, A. Zrelli⁴, Regina Fátima Moreira¹

¹*Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Florianopolis, Brazil*

²*Departamento de Química Inorgánica, Instituto Interuniversitario de Investigación en Biorrefinerías I3B, Universidad de Málaga, Málaga, España. E-mail:castellon@uma.es*

³*Departamento de Ingeniería Química, Escuela de Ingeniería Industrial, Universidad de Málaga, Málaga, España*

⁴*Research Unit Advanced Materials, Applied Mechanics, Innovative Processes and Environment, UR22ES04, Higher Institute of Applied Sciences and Technology of Gabes (ISSAT), University of Gabes, Gabes, Tunisia*

Innovative electrospun poly(vinyl alcohol) (PVA)–geopolymer–zeolite 13X composite membranes were successfully fabricated and systematically characterized. The optimal electrospinning solution was prepared by mixing ethanol with 8 wt.% PVA and 1wt.% of inorganic powder (geopolymer, zeolite13X, or geopolymer/zeolite composites containing 20 or 30 wt.% zeolite). The incorporation of the inorganic fillers into the PVA matrix led to significant improvements in thermal, mechanical, and adsorption properties. Thermogravimetric analysis (TGA) showed delayed degradation with differential thermal gravimetric analysis (DTG) peaks shifting from 293C (MGP) to 313C (MZ30), with total mass losses between 92.7 and 94.0%. Mechanical testing revealed that MGP exhibited the highest tensile strength (2.81 MPa) and elongation (227.8%), while MZ30 presented 1.72M Pa strength with improved flexibility (62.1% strain) compared to MZ20 (34.9%). Nitrogen physisorption analysis indicated surface areas ranging from 2.4 m²/g (MZ) to 24.3m²/g (MZ30), with fibre diameters spanning 10.7–44.4 µm. Gas adsorption studies demonstrated that hydrogen uptake increased from 0.01 mmol/g in pure PVA to 0.08 mmol/g in MZ30, and CO adsorption improved from 0.03 to 0.08 mmol/g. In contrast, CO₂ uptake remained largely unchanged, with values between 0.21–0.66 mmol/g, close to that of pure PVA (0.66 mmol/g). These results confirm that even at low filler content, the hybrid membranes display enhanced multifunctional performance, making them promising candidates for separation processes, filtration, catalytic supports, and protective coatings.

Introduction

Membrane-based systems, especially those using polyvinyl alcohol (PVA), offer effective solutions for separation processes due to their beneficial properties, such as hydrophilicity, biodegradability, and low cost. PVA enhances membrane performance by improving permeability and antifouling in aqueous applications, while also supporting environmentally friendly fabrication. PVA-based membranes are applied in pervaporation, dialysis, fuel cells, water purification, and gas separation. Therefore, due to its affordability and adaptability, electrospinning has emerged as a very promising method for creating polymer composite nanofibres. This technique allows controlling the shape of the resulting nanofibres and enables the production of composites with predetermined porosity and surface area. So, the incorporation of inorganic fillers, such as zeolites and geopolymers, improves their structural, thermal, and transport properties, thus expanding their potential applications.

Results

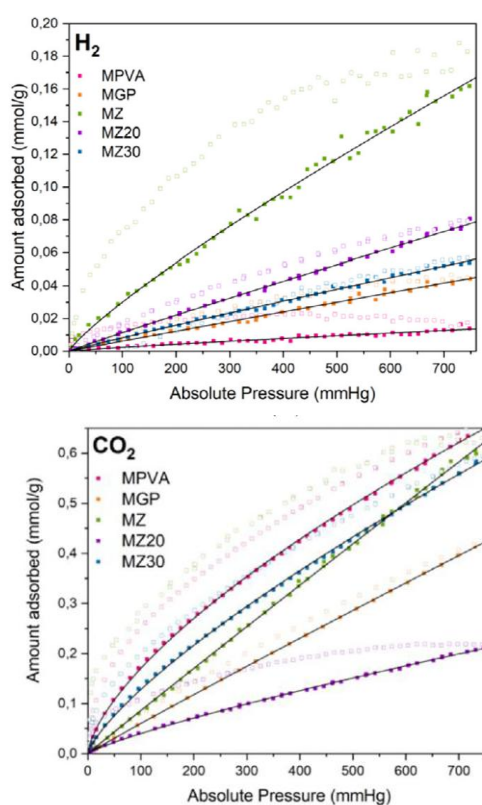


Figure 1. Adsorption isotherms of different pure H_2 and CO_2 on the electrospun membranes (closed squares are for adsorption; open squares for desorption isotherms; lines indicate the Freundlich isotherm model fittings).

The adsorption capacity of a material depends on many factors, like surface area, volume, density, pore size and volume, and interpore connectivity. The H₂, and CO₂ adsorption equilibrium isotherms at 30 °C with pressure ranging from 0 to 760 mm Hg are shown in Figure 1. Different mathematical models (Langmuir, Freundlich, Temkin, Sips, and Redlich Peterson) were applied for the analysis of the experimental data; however, the model that best fit the experimental isotherms data was the Freundlich model ($R^2 \geq 0.994$), which is one of the first empiric equations used to describe equilibrium data. This model describes the equilibrium on heterogeneous surfaces and considers that the heat of adsorption occurs exponentially from the monolayer

Conclusions

This work validates electrospinning as an effective route to prepare polymer/inorganic composite membranes and provides the groundwork for further optimization. Increasing the filler content, improving dispersion, and tailoring electrospinning conditions are promising strategies for expanding the functional performance of these materials toward practical applications in CO₂ capture and gas separation. capacity.

Acknowledgements

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P16. COMPETITIVE ADSORPTION OF H₂O, CO₂ AND CH₄ ON CHA ZEOLITE: INSIGHTS FROM MULTICOMPONENT BREAKTHROUGH EXPERIMENTS.

Beatriz Oliveira Nascimento¹, Yasmin Dafne Moreira Duarte¹, Rafaelle Gomes Santiago^{1,2}, Débora Aline Soares Maia¹, Antônio Eurico Belo Torres¹, Dárley Carrijo de Melo³, Diana Cristina Silva de Azevedo¹, Moisés Bastos-Neto^{1*}

¹ Laboratório de Pesquisa em Adsorção e Captura de CO₂ – Federal University of Ceará (UFC), Fortaleza, 60.455-900, Brazil.

² Energy Engineering Division, Aeronautics Institute of Technology (ITA), Fortaleza-CE, 60415-513, Brazil.

³ Petrobras/CENPES, Rio de Janeiro, 21.941-915, Brazil.

* mbn@ufc.br

Natural gas dehydration was investigated through mono- and multicomponent breakthrough experiments involving H₂O, CO₂ and CH₄ on a CHA-type zeolite. While breakthrough times were only slightly affected by multicomponent operation, water strongly influenced adsorption behavior, suppressing the adsorption of CO₂ and CH₄ through competitive adsorption and displacement effects. The results highlight the dominant role of H₂O and provide valuable insights for the design of TSA processes for natural gas dehydration.

Introduction

Water removal is a critical step in natural gas processing because moisture can cause corrosion, hydrate formation and operational issues. CHA zeolites are promising adsorbents for natural gas dehydration. However, quantitative information on the competitive adsorption of water and natural gas components remains scarce. Although TSA is widely employed for dehydration [1], the design of adsorption units requires a detailed understanding of multicomponent adsorption phenomena involving H₂O, CO₂ and CH₄. Therefore, this work investigates mono- and multicomponent breakthrough behavior on a CHA-type zeolite.

Experimental

In this study, a CHA-type zeolite was used as adsorbent. The material was characterized by X-Ray diffraction (XRD), N₂ adsorption/desorption at 77 K and CO₂ adsorption at 273 K. Equilibrium adsorption isothermal at 303 K were measured for H₂O, CO₂ and CH₄ to be able to compare with the dynamic outcomes at the same conditions. Measurements were carried out using an IGA 02 (Hiden Isochema, UK) for water vapor and Autosorb iQ₃ (Quantachrome Instruments, USA) for the CO₂ and CH₄. Prior to all adsorption experiment, the sample was degassed at 573 K under vacuum for 10 h. Breakthrough curves were obtained in a MixSorb S (3P, Germany), in which the column

had an inner diameter of 0,43 cm and a length of 2 cm. The system was equipped with four Mass Flow Controller (MFCs). A vapor generator, through which helium was passed as carrier gas, was installed upstream of the MFCs. The column effluent stream was monitored by an online mass spectrometer (MKS Instruments, UK).

Results and Discussion

Table 1 summarizes the breakthrough results. The feed composition was adjusted to a CO₂/CH₄ molar ratio of 1:4, corresponding to 6 and 24 mol%, respectively. Water vapor concentration was fixed at 0.49 mol% using a saturated stream, while helium was employed as diluent in both single- and multicomponent experiments.

Breakpoint times, defined as the moment at which the outlet concentration reached 5% of the inlet concentration, showed little variation between single- and multicomponent runs. In contrast, significant differences were observed in the adsorption capacities. While H₂O adsorption was only slightly affected by the presence of CO₂, the adsorption capacities of both CO₂ and CH₄ became negligible under multicomponent conditions. This behavior is attributed to the much stronger affinity of the CHA zeolite for water. As the water adsorption front propagates through the bed, it progressively displaces the more weakly adsorbed species from the adsorption sites, generating pronounced roll-up effects in the breakthrough curves. Consequently, the net adsorbed amounts of CO₂ and CH₄ became negligible in the multicomponent experiments, evidencing the dominant role of water in determining the dynamic adsorption behavior of the system [2].

Table 1. Summary of the single and multicomponent breakthrough experiments.

Adsorbate	Breakpoint time (s)	Partial pressure (bar)	Adsorbed amount (mmol g ⁻¹)
CO ₂	696.5	0.06	1.90
CH ₄	55.7	0.25	0.04
H ₂ O	33621.7	0.005	7.16
CH ₄ / CO ₂	56.6 / 695.7	0.25 / 0.06	0.0 / 1.86
CO ₂ / H ₂ O	729.3 / 33208.2	0.062 / 0.005	0.0 / 6.973

Conclusion

The breakthrough experiments demonstrated the strong preferential adsorption of H₂O on the CHA zeolite. Under multicomponent conditions, the adsorption of CO₂ and CH₄ became negligible due to competitive adsorption and displacement by water, resulting in pronounced roll-up effects. These findings highlight the importance of accounting for

multicomponent adsorption phenomena in the design of TSA units for natural gas dehydration.

Acknowledgments

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P17. INTEGRATED BIOHYDROGEN UPGRADING AND CO₂ CAPTURE USING ALPO-22 IN A VACUUM SWING ADSORPTION PROCESS.

Enrique Vilarrosa-Garcia¹, Antônio Eurico Belo Torres¹, Bianca Ferreira dos Santos¹, Débora Aline Soares Maia¹, José Carlos Alexandre de Oliveira¹, Sebastião Mardônio Pereira de Lucena¹, Diana Cristina Silva de Azevedo¹, Moisés Bastos-Neto^{1*}

¹ Laboratório de Pesquisa em Adsorção e Captura de CO₂ – Federal University of Ceará (UFC), Fortaleza, 60.455-900, Brazil

*mbn@ufc.br

Biohydrogen streams contain significant amounts of CO₂ that must be removed before H₂ utilization. This work evaluates an ALPO-22 adsorbent in a two-column VSA process for simultaneous hydrogen purification and CO₂ capture. Dynamic simulations predicted H₂ purity and recovery of 98.2% and 99.3%, respectively, together with a CO₂ product stream reaching 98.8% purity and 93.9% recovery. These results demonstrate the potential of ALPO-22 for integrated biohydrogen upgrading and carbon capture.

Introduction

Biological hydrogen production routes, such as dark fermentation, typically generate gas streams containing significant amounts of CO₂, requiring downstream purification before hydrogen utilization [1]. Adsorption-based processes have emerged as attractive alternatives to conventional amine scrubbing due to their lower energy requirements, operational flexibility, and potential for simultaneous hydrogen purification and CO₂ capture [2]. Among the available adsorbents, aluminophosphates are particularly attractive due to their tunable pore structures and favorable regeneration characteristics. Therefore, the present work evaluates the performance of ALPO-22 in a VSA process for simultaneous biohydrogen upgrading and CO₂ capture.

Methodology

The adsorbent investigated in this work was an AWW-type zeolite, as classified by the International Zeolite Association (IZA) Structure Commission database. CO₂ and H₂ adsorption equilibrium isotherms were measured at 298, 323, and 343 K and 298 K respectively, and fitted using the Sips model. The resulting parameters were incorporated into a dynamic cyclic adsorption model. A two-column, four-step Vacuum Swing Adsorption (VSA) cycle was simulated for the separation of a 40/60 mol% CO₂/H₂ mixture at 298 K. The cycle consisted of adsorption, co-current depressurization, counter-current evacuation, and pressurization. Simulations were performed for a packed bed of 0.5 m length and 0.08 m diameter operating at a feed flow rate of 3.6 NL min⁻¹. The adsorption step was evaluated for adsorption times ranging from 300 to 1000

s, while the cycle operated between a high pressure (PH) of 1.0 bar, an intermediate pressure (PI) of 0.4 bar, and a low pressure (PL) of 0.01 bar (Figure 1)

Results and Discussion

The CO₂ adsorption isotherms confirmed the affinity of AlPO-22 toward CO₂ over the investigated temperature range and were accurately described by the Sips model. The resulting equilibrium parameters provided a reliable basis for the dynamic simulation of the VSA process.

Figure 2 shows the effect of adsorption time on the separation performance for an intermediate pressure of PI= 0.4 bar. Increasing the adsorption time from 300 to 1000 s increased CO₂ purity from 94.3 to 98.8%, while CO₂ recovery decreased slightly from 97.2 to 93.9%. Conversely, H₂ purity increased from 96.1 to 98.2% as the adsorption time decreased, with H₂ recoveries ranging from 96.2 to 99.3%.

The higher CO₂ purity obtained at longer adsorption times can be attributed to the more extensive utilization of the adsorption bed, resulting in higher CO₂ loading prior to evacuation. In contrast, shorter adsorption times limited the propagation of the CO₂ mass-transfer zone, favouring higher H₂ purity and CO₂ recovery. These results reveal the expected trade-off between purity and recovery and demonstrate the strong influence of operating conditions on process performance.

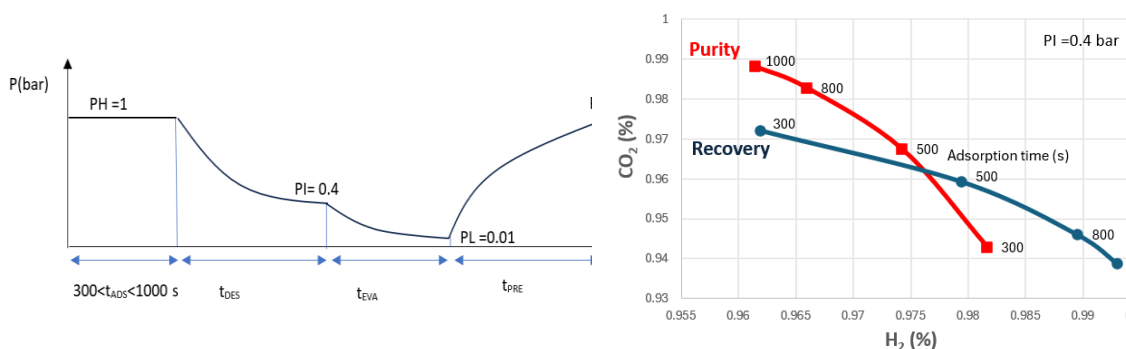


Figure 1. Schematic representation of the four-step VSA cycle used for CO₂/H₂ separation

Figure 2. Trade-off between CO₂ purity and recovery as a function of H₂ purity for different adsorption times in the VSA separation of a 40/60 mol% CO₂/H₂ mixture.

Conclusions

An AWW-type aluminophosphate was evaluated as an adsorbent for the separation of CO₂/H₂ mixtures representative of biohydrogen production streams. The proposed two-column, four-step VSA process achieved H₂ purities and recoveries of up to 98.2% and 99.3%, respectively. These results demonstrate the feasibility of simultaneously

upgrading biohydrogen and capturing a concentrated CO₂ stream. Furthermore, the favorable regeneration characteristics and S-shaped water vapor adsorption behavior of AlPO-22 suggest potential advantages for future applications involving humid biohydrogen streams.

Acknowledgments

The authors gratefully acknowledge the financial support provided by CNPq, linked to the Brazilian Ministry of Science, Technology and Innovation (MCTI); CAPES, linked to the Brazilian Ministry of Education (MEC); and FINEP (Financial Agency for Studies and Projects).

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P18. HIGH-TEMPERATURE ADSORPTION OF CO₂ AND CH₄ ON COMMERCIAL 4A ZEOLITE: EQUILIBRIUM AND KINETIC INSIGHTS FOR TSA DESIGN.

Vitória Natasha Silva Oliveira¹, Antônio Eurico Belo Torres¹, Rafaelle Gomes Santiago^{1,2*}, Moises Bastos-Neto^{1*}

¹ *Laboratório de Pesquisa em Adsorção e Captura de CO₂ - Universidade Federal do Ceará, Campus do Pici, Fortaleza-CE, 60455-760, Brazil.*

² *Energy Engineering Division, Aeronautics Institute of Technology (ITA), Fortaleza-CE, 60415-513, Brazil.*

* *rafaelleg@gmail.com*

Commercial 4A zeolites are widely employed for natural gas dehydration by TSA, where the adsorbent is exposed not only to water vapor but also to major gas components such as CH₄ and CO₂. Reliable equilibrium and kinetic data over broad temperature ranges, including regeneration conditions, remain scarce despite their importance for realistic process simulations. Therefore, this work presents equilibrium and kinetic data for CO₂ and CH₄ adsorption on a commercial 4A zeolite from 25 to 250 °C. The resulting thermodynamic and kinetic parameters provide a basis for future multicomponent studies and the design of industrial TSA units.

Introduction

Commercial 4A zeolites are widely employed in natural gas dehydration by TSA due to their high water affinity, thermal stability and industrial maturity. During operation, however, the adsorbent is continuously exposed to other gas components, particularly CH₄ and CO₂, whose adsorption behavior may influence process performance and must be considered in realistic process simulations. Despite their relevance, equilibrium and kinetic data for these gases on 4A zeolites over the wide temperature range encountered during adsorption and regeneration cycles remain scarce. Therefore, this work presents equilibrium and kinetic measurements of CO₂ and CH₄ adsorption on a commercial 4A zeolite from 25 to 250 °C, providing a basis for future multicomponent studies and TSA process modeling.

Materials and methods

Single-component adsorption isotherms for CO₂ (0.17–10 bar) and CH₄ (0.25–35 bar) were measured gravimetrically from 25 to 250 °C using a Rubotherm Magnetic Suspension Balance (± 0.02 mg reproducibility). Prior to analysis, *ca.* 0.8 g of commercial zeolite 4A pellets were regenerated in situ at 300 °C under vacuum (0.01 bar) for 10 h. Isotherms were obtained via sequential gas dosing until equilibrium, while mass uptake

over time was recorded for kinetic analysis. All mass signals were corrected for buoyancy. Equilibrium data were correlated using the Sips equation, and the isosteric heat of adsorption was calculated via the Clausius-Clapeyron approach. Adsorption kinetics were evaluated using the Linear Driving Force (LDF) model applied to the uptake curves obtained at 25 and 250 °C (10 bar for CO₂ and pressures above 25 bar for CH₄) [1].

Results

Representative adsorption isotherms for CO₂ and CH₄ on 4A zeolite are shown in Figure 1. The Sips model accurately described the equilibrium data over the entire temperature range investigated (25–250 °C), with average RMSE values of 0.08 mmol g⁻¹ for CO₂ and 0.04 mmol g⁻¹ for CH₄.

For both gases, adsorption capacity decreased with increasing temperature, consistent with the exothermic nature of physisorption. However, CO₂ exhibited significantly higher adsorption capacities than CH₄, particularly at low pressures, owing to its higher critical temperature and stronger interaction with the zeolite framework [2].

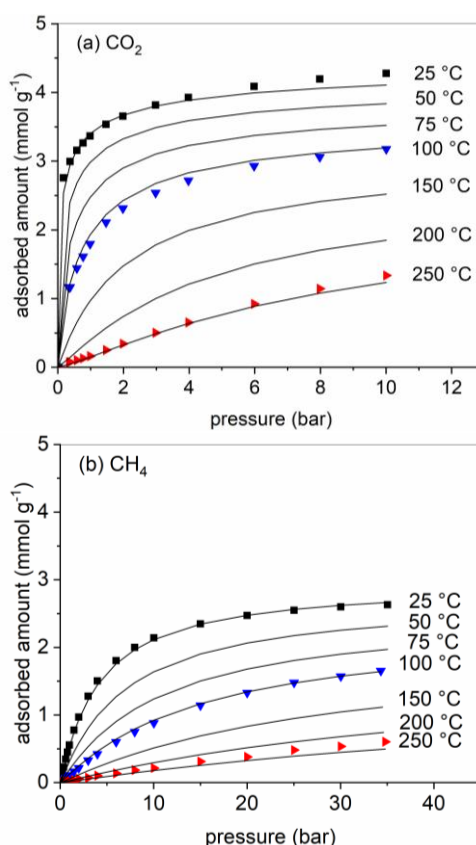


Figure 1. Experimental and Sips model adsorption isotherms of CO₂ (a) and CH₄ (b) on 4A zeolite at different temperatures.

The isosteric heats of adsorption ranged from 35–37 kJ mol⁻¹ for CO₂ and 20–24 kJ mol⁻¹ for CH₄, confirming the greater affinity of the adsorbent for CO₂. Kinetic analyses yielded average k_{LDF} values of 0.0129 s⁻¹ and 0.0028 s⁻¹ for CO₂ and CH₄, respectively, corresponding to a kinetic selectivity of 4.6. Together, these results provide equilibrium and kinetic parameters over adsorption and regeneration temperatures relevant to TSA operation.

Conclusions

A comprehensive equilibrium and kinetic dataset for CO₂ and CH₄ adsorption on commercial 4A zeolite was obtained over a wide temperature range (25–250 °C). CO₂ exhibited significantly higher adsorption affinity and faster adsorption kinetics than CH₄, as confirmed by the equilibrium isotherms, isosteric heats of adsorption and kinetic selectivity. These results provide key parameters for future multicomponent investigations and the realistic modeling of TSA processes for natural gas treatment.

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P19. Scalable and Robust Metal Organic Frameworks for Cultural Heritage Preservation.

Miguel Vitoriano Teixeira^{1,*}, Tarik Aaboub², Abeer Mohtar¹, Farid Nouar², Vanessa Pimenta², Georges Mouchaham², Christian Serre², Moisés Pinto¹

¹*Instituto Superior Técnico (IST), CERENA –Centro de Recursos Naturais e Ambiente, Avenida Rovisco Pais, 1, 1049-001 Lisboa, Portugal.*

²*Institut des Matériaux Poreux de Paris, UMR CNRS 8004, ENS, ESPCI, PSL University, 75005 Paris, France miguel.vitoriano.teixeira@tecnico.ulisboa.pt*

Metal Organic Frameworks (MOFs) are being evaluated as high performance adsorbent materials for volatile organic compounds (VOCs) removal in cultural heritage (CH) preservation context. To enable their application at large scale a scalable reproducible and green synthesis route must be followed. MOFs were synthesized at lab-scale and using a scaled-up protocol using friendly synthesis conditions. The structure and properties of MOFs were characterized by various methods like XRD, FTIR, TGA and SEM. Furthermore, to determine their acetic acid adsorption capacity, single component acetic acids isotherms were performed. In addition, to assess the adsorption under ambient conditions, i.e in the presence of moisture, environmental chamber experiments were performed. After the identification of the most efficient MOFs in capturing acetic acid under moisture conditions, the synthesis route and post-synthesis treatment factors were analysed. The best-performing samples reduced total VOCs (TVOCs) levels to near baseline within 100 minutes in the environmental chamber proving to be extremely efficient even at low concentrations of acetic acid in the presence of moisture.

Introduction

Air pollutants such as hydrogen sulphide (H₂S), formaldehyde, acetic acid and nitrogen oxides (NO_x) pose a significant risk to CH objects stored in galleries, Libraries, Archives and Museums (GLAMs). Long-term exposure to these VOCs compromises the preservation of artefacts. MOFs are highly porous crystalline materials, with high surface areas with tailorable pore chemistry, making them promising materials for VOCs adsorption. The SIMIACCI projects aims to develop a smart predictive maintenance tool, combining real time environmental sensor data, adsorbent properties and CH object properties to generate scenario-based recommendations for GLAMs institutions. The present work focuses on the experimental characterisation of different MOFs for acetic acid adsorption. In parallel, different deep learning models are being developed and tested to forecast indoor VOCs concentrations, integrating

data such as temperature, relative humidity and material emission rates into the SMART HUB prediction module.

Experimental

Following structure confirmation, Several MOFs families were selected and tested for acetic acid. Adsorption isotherms were obtained using a microbalance system under vacuum. Adsorption behaviour was also assessed in a custom environmental chamber purged with nitrogen (N₂) to ensure a VOC-free chamber and conditioned at 40% relative humidity. In parallel, a bivariate emission surface $E(T, RH)$ was fitted to experimental emission data for formaldehyde, and a ConV1D + GRU deep learning architecture was trained using T, RH, emission rate and VOC vapour pressure as exogeneous inputs, with 5-fold cross validation applied to ensure robust evaluation.

Results and Discussion

MIL-100 (Fe) MOF was identified as highly efficiency MOF for capturing acetic acid in the presence of moisture [1]. Where it was proven that the acetic acid can replace water molecules coordinated at the open metal sites. The application of this MOF in-field in the case of archives showed very promising behaviour [2]. Currently, various scale-up routes are being tested to synthesis MIL-100(Fe) and their application in the context of cultural heritage preservation to be studied in galleries, libraries, archives and museums. Other Fe-based MOFs synthesised from cost-effective commercially available ligands are also being tested, and the results will be showed. Regarding the predictive modelling, the ConV1D + GRU model achieved a cross-validation correlation of $R = 0.94 \pm 0.02$, demonstrating strong generalisation for indoor VOCs forecasting.

Conclusions

In conclusion scale-up of MIL-100 is being successful and reproducible with several kg-scale. Alternative MOFs are being studied, and other scale-up protocols are being developed. The experimental data will be integrated into the SIMIACCI SMART HUB to support predictive maintenance and conservation recommendations. Future work will involve the testing of other target pollutants (NO_x, H₂S, formaldehyde).

Acknowledgments

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P20. Hydrogen recovery from off-gases with nitrogen-rich impurity by pressure swing adsorption using NaX and CaX zeolites.

Álvaro Trujillo^{1,2}, Ernesto Simón², Rubén Calero¹, V.Ismael Águeda¹, José Antonio Delgado^{1,*}

¹*Catalysis and Separation Processes Group (CyPS), Chemical and Materials Engineering Department, Universidad Complutense de Madrid, 28040 Madrid, Spain;*

²*Técnicas Reunidas Internacional. Av. Burgos 89, Edificio Adequa 5, 3a planta. 28050, Madrid, Spain;*

**jadeldob@ucm.es*

Introduction

Global hydrogen demand reached almost 100 Mt in 2024. Hydrogen produced from non-fossil fuels is expected to play a key role in efforts to reduce dependence on fossil fuels in sectors where it is difficult to cut emissions [1]. Steam methane reforming (SMR) is currently the most common method of producing hydrogen on a commercial scale. Hydrogen can also be obtained from coke oven gas (COG), which is generated during the coking process in steel production. Major impurities in COG are methane, nitrogen, carbon monoxide and carbon dioxide where the typical concentration of nitrogen is about 10 % v/v. [2, 3]. Several adsorbents based on zeolites (X or A) have been used in the hydrogen purification by means adsorption using PSA technology. The aim of this work is to evaluate the influence of the exchange cation (Na or Ca) in the hydrogen purification of COG by means of PSA.

Experimental

NaX and CaX were the two different industrial zeolites with FAU structure tested in this work. The adsorbents in pellet form were characterized using XRD, XRF, TG, N₂ adsorption-desorption isotherms at 77K, and helium pycnometry. Adsorption equilibrium isotherms of CO, N₂, CO₂ and CH₄ were measured using a BELSORP MAX II volumetric equipment at 25C-65C. Breakthrough curves were measured and the kinetic parameters were obtained using a mathematical model. A Pressure Swing Adsorption process was simulated using PSASIM® [4].

Results and Discussion

The adsorbent NaX and CaX presented a FAU structure. In the sample NaX the exchange cation is sodium while in CaX the main exchange cation is calcium and a low amount of sodium. Both industrial adsorbents are stable till 350°C. From the nitrogen adsorption-desorption isotherm at 77K it can be concluded that these adsorbents presented micropores and macropores.

In Table 1 the fitting parameters to the Dual Langmuir Model of the equilibrium adsorption isotherms are presented ($q = q_{\max 1} \cdot b_1 \cdot p / (1 + b_1 \cdot p) + q_{\max 2} \cdot b_2 \cdot p / (1 + b_2 \cdot p)$; $b_1 = b_{01} \cdot \exp(\Delta_1 / T)$; $b_2 = b_{02} \cdot \exp(\Delta_2 / T)$).

Table 1-. Dual Langmuir Model fitting parameters.

SAMPLE	GAS	$q_{\max 1}$ (mol kg ⁻¹)	$q_{\max 2}$ (mol kg ⁻¹)	b_{01} (Pa ⁻¹)	b_{02} (Pa ⁻¹)	Δ_1 (K)	Δ_2 (K)	K_H 298K, mol kg ⁻¹ Pa ⁻¹
NaX	CO	2.58	0	4.78E-10	0	2785	0	1.41E-05
	CO ₂	1.88	3.19	5.58E-11	1.10E-10	5391	4016	7.79E-03
	CH ₄	5.89	0	1.09E-09	0	2033	0	5.89E-06
	N ₂	3.04	0	9.61E-10	0	2114	0	3.52E-06
CaX	CO	1.29	2.09	8.94E-11	4.50E-10	4627	2540	6.43E-04
	CO ₂	1.14	4.64	1.18E-10	4.11E-11	5155	3953	4.49E-03
	CH ₄	1.62	0	4.38E-10	0	3366	0	5.71E-05
	N ₂	1.52	0	2.28E-10	0	3517	0	4.63E-05

As can be seen in the table both adsorbents present higher affinity (K_H) to CO₂. Nitrogen is the most difficult molecule to in the COG mixture. The affinity for nitrogen is higher in CaX than in NaX zeolite, which could lead to a better PSA performance.

Acknowledgments

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P21. Assessing biochar pore development by O₂ adsorption at 77K.

Ignacio Campello Gómez¹, José María Sánchez Rodas¹, Kiara Montiel Centeno¹, Cristina Gutiérrez Muñoz¹

¹Centro Ibérico de Investigación en Almacenamiento Energético (CIIE)

*cristina.gutierrez@ciiae.org

Porosity development in biochar is commonly characterized by N₂ adsorption isotherms at 77K. However, limited accessibility to narrow micropores may lead to an incomplete description of the pore network, particularly in poorly activated or highly microporous carbons. In this work, O₂ adsorption at 77K was evaluated as a complementary approach for assessing pore development in biochars prepared from two agricultural residues, nutshell and rockrose pyrolyzed at 500 and 800 °C after different pre-pyrolysis washing treatments. O₂ isotherms reveal porosity features undetected by N₂ analysis, providing more accurate BET surface area values and pore size distribution. These results demonstrate the potential of O₂ adsorption as a sensitive and time-efficient approach to complement or replace N₂ analysis in the characterization of narrow porosity biochar materials, and help to better understand the pore development process during pyrolysis of biomass.

Introduction

Biochar materials derived from agricultural residues represent a promising approach for the valorization of waste biomass. Although washing of raw precursors prior to pyrolysis is a common practice, its effects on pore development have not been systematically addressed. Furthermore, while it is generally accepted that pyrolysis under N₂ atmosphere leads to limited porosity development [1], the underlying mechanisms remain poorly understood. Characterization of these materials is typically performed by N₂ adsorption isotherms at 77K, given the higher cost of Ar isotherms at 87K. O₂ adsorption at 77K has emerged as a valuable alternative [2,3], owing to its smaller kinetic diameter, low quadrupole moment, and ready availability, making it particularly suitable for the characterization of narrow microporosity in biochar [4]. In this work, the effect of different solvent washing treatments prior to pyrolysis has been systematically studied for two agricultural residues: nutshell (*Juglans regia*) and rockrose (*Cistus ladanifer*).

Experimental

Rockrose (J) and nutshell (NS) biomass precursors were subjected to different washing pretreatments prior to pyrolysis: washing with water (W), with a

water:isopropanol:cyclohexane (WIC, 1:3:1, v/v/v), and with cyclohexane (C) under stirring for 72 h at room temperature. After washing, the solids were dried and pyrolyzed under N₂ atmosphere at 500 and 800°C to obtain biochar, and their porosity was characterized by N₂, O₂ and CO₂ adsorption isotherms at 77 and 273K, respectively, while the structural characterization was performed by Raman spectroscopy, FTIR and thermogravimetric analysis.

Results

O₂ adsorption at 77 K reveals substantial accessible surface area in all analysed biochars, including samples showing limited or negligible N₂ adsorption. CO₂ isotherms confirm the presence of narrow microporosity across all samples, with adsorption values exceeding 1.5 mmol/g. Water washing caused a marked increase in pore development: BET surface area nearly doubled upon water washing at 800°C, while total pore volume increased by a factor of 3 relative to the other washing protocols, accompanied by a greater mesopore contribution. Fig. 1 compares the influence of the pretreatment (W and WIC) on porosity, showing predominantly very narrow micropores with WIC washing. C washing moderately increased BET surface area and total pore volume, promoting limited mesopore formation. These results demonstrate that a high degree of porosity tuning is achievable through simple adjustments to the pre-pyrolysis washing step. O₂ isotherms further revealed that the BET surface area was far from negligible in samples where N₂ adsorption was minimal, a consequence of very narrow micropores inaccessible to N₂ under these conditions, as shown in Fig. 1.

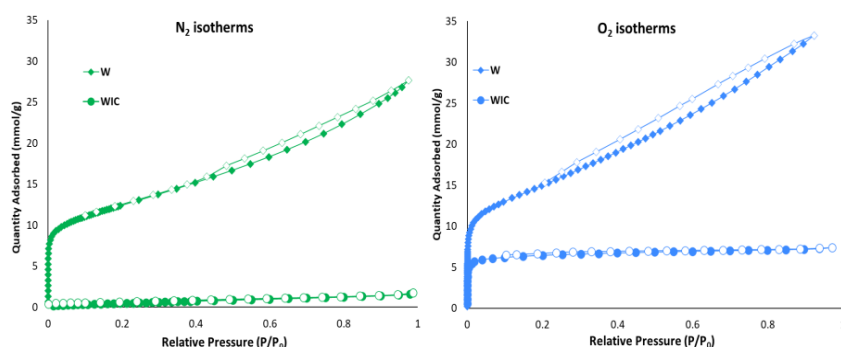


Figure 1. Isotherms of NS with different washing methods (W & WIC) for N₂ (left) and O₂ (right) pyrolysed at 800°C.

Omission of O₂ analysis would therefore have led to erroneous conclusions regarding the textural properties of these materials. Raman spectra of biochar samples are highly similar at a given pyrolysis temperature, regardless of the washing treatment. Confirming that pyrolysis mechanisms are essentially unaffected by the washing protocol. FTIR spectra of washed precursors show only minor differences among

pretreatments. These results suggest that washing protocols do not significantly alter the structural or surface composition of the solid precursors, nor the carbon structural features developed during the pyrolysis.

Conclusions

Washing pre-treatments significantly affect pore development in biochars derived from nutshell and rockrose, with water washing leading to the highest surface areas and pore volumes, especially at 800°C. O₂ adsorption at 77K proves highly sensitive to narrow porosity that may be underestimated by conventional N₂ adsorption. The results indicate that O₂ isothermal analysis at 77K is a promising method for studying the porosity of biochar materials, allowing to reveal porosity which remains non-accessible for N₂ molecules. Raman and FTIR analyses indicate that washing does not substantially modify the carbon structural framework. Overall, biomass washing provides a simple and effective route to tune biochar pore accessibility and architecture.

Acknowledgments

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P22. Tailored Al-PILCs for CO₂ Capture: Optimisation and Performance in Pressure Swing Adsorption for Cement Emissions.

¹ CERENA, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, No. 1, 1049-001 Lisboa, Portugal.

² CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.

* taniafrade@tecnico.ulisboa.pt

Introduction

The removal of carbon dioxide (CO₂) from flue gases emitted by cement plant sources is a key step toward full decarbonization of the sector. Adsorption-based processes using solid adsorbents are among the most promising technologies. However, their large-scale implementation requires the development of efficient materials derived from cost-effective, sustainable resources. In this context, pillared clays (PILCs) have emerged as attractive candidates. Previously, we have demonstrated that Zirconium-pillared interlayered clays (Zr-PILCs) show promising performance for CO₂ capture from cement plant flue gases, with relatively low estimated separation costs [1]. Additionally, these materials can be synthesised from abundant natural clays under mild conditions using water as a solvent, thereby supporting their scalability. Despite these advantages, important challenges remain for industrial applications, namely the production of Zr-PILCs at large-scale and the need to ensure their stability in the presence of flue gas impurities. Recently, we demonstrated scaled-up production of Zr-PILCs with reduced water volume and shorter washing times, which were shown to be highly stable in the presence of flue gas contaminants such as SO₂, HCl, and NH₃. Additionally, these PILCs were applied in a two-stage six-bed vacuum pressure swing adsorption (VPSA) process for a CO₂/N₂ gas mixture, achieving 97% and 98% of purity and recovery of CO₂, respectively, with an energy consumption of 0.4 MWh/ton CO₂ removed [2]. Even though it showed a real opportunity for industrial-scale implementation, the cost of zirconium precursors may increase CAPEX, which could be a drawback for industrial production.

Aluminium-pillared clays (Al-PILCs) offer several advantages over Zr-PILCs for industrial applications, primarily due to their lower cost, greater availability of raw materials, and straightforward, scalable synthesis. In addition, Al-PILCs exhibit good thermal and hydrothermal stability and have been extensively studied, providing well-established performance and reliability in adsorption processes [3]. These factors make Al-PILCs more attractive for large-scale applications such as CO₂ capture, where economic

feasibility and process robustness are critical.

Experimental

In the present work, we demonstrate an optimisation of the Al/clay ratio and its scalability to the kilogram scale, using $\text{Al}(\text{NO}_3)_3$ as the Al precursor rather than the typical AlCl_3 , which will allow for more controlled hydrolysis and formation of Al polycations, facilitating the synthesis of well-defined pillared structures. To confirm that Al-PILCs can serve as robust materials for flue gas CO_2 separation in the extrudate form, we conducted a thorough assessment of their adsorption performance, collecting experimental data on both pure components and gas mixtures under various conditions. This data was instrumental in developing precise process simulation models that effectively describe the separation of flue gas components. Furthermore, we utilised these models to optimise the design of PSA processes for separating CO_2 from N_2 , to yield critical performance indicators, and to conduct sensitivity analysis.

Results and Final Remarks

The preliminary adsorption results obtained with this Al-PILC are very promising, as the adsorbed amounts are very close to those from the Zr-PILC [2] (Figure 1). The separation of CO_2 from CO_2/N_2 mixtures was demonstrated using breakthrough experiments at pressures ranging from 1 to 3 bar. The adsorbed amounts obtained from gas mixtures confirmed the estimations made from the pure compounds' adsorption isotherms using the ideal adsorbed solution theory. The information obtained from these experiments and equilibrium isotherms was used to study the application of cyclic adsorption PSA with 6 columns and 18 steps, which previously yielded promising results for Zr-PILCs.

The optimised Al-PILCs exhibit promising adsorption performance for CO_2 capture from flue gases. Their synthesis from natural clays via water-based processes under ambient pressure and mild temperatures makes Al-PILCs a cost-effective and environmentally sustainable option for large-scale adsorption systems. Furthermore, preliminary process design, supported by validated models, indicates that Al-PILCs can achieve high CO_2 purity and recovery in cyclic separation processes, highlighting their potential for practical deployment in flue gas treatment.

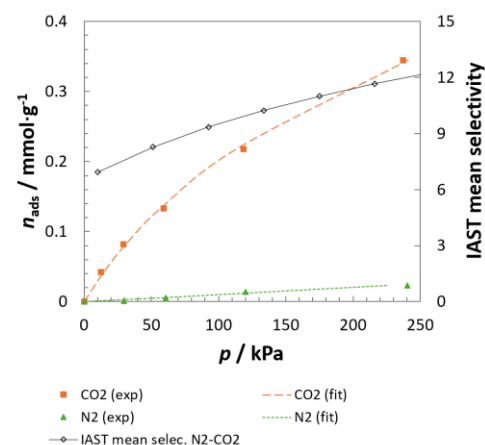


Figure 1 – Adsorption isotherms of pure gases of CO₂ and N₂ at 25 °C, and selectivity for the separation of CO₂ from N₂ of the adsorption of CO₂/N₂ mixtures with Al-PILCs.

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P23. ESTUDIO DE ADSORCIÓN DE HIDROCARBUROS LIGEROS EN SILICALITA-2 MEDIANTE DIFRACCIÓN DE RAYOS X IN-SITU

Alberto Barros, Silvia Martí, Miguel Palomino, José L. Jordá, Fernando Rey, Susana Valencia*

Instituto de Tecnología Química (ITQ), Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, 46022-Valencia (España).

* svalenci@itq.upv.es

En este estudio se ha analizado la flexibilidad estructural de la zeolita Silicalita-2 mediante adsorción de hidrocarburos ligeros seguida por difracción de rayos X in-situ. Los resultados indican que, contrariamente a lo que ocurre en otras zeolitas, en Silicalita-2 no se da un cambio de fase durante la adsorción, puesto que se mantiene la misma simetría, sino que se produce un aumento del volumen de la celda unidad que sugiere una expansión elástica de la estructura debida a la presión ejercida sobre las paredes de los poros zeolíticos.

Introducción

Los cambios estructurales de zeolitas durante procesos de adsorción se han descrito previamente para MFI [1], RHO [2] y varios aluminofosfatos [3,4], entre otros. Estas modificaciones estructurales generalmente implican un incremento de la capacidad de adsorción por encima de cierta presión, evidenciado por el aumento abrupto en la isoterma de adsorción a cierta presión. Esto se acompaña de la aparición/desaparición de picos de difracción de rayos X, lo que indica una transición de fase sin cambios en la conectividad atómica (es decir, un cambio de simetría). Además, este cambio de fase no depende únicamente de la presión del gas, sino también de la naturaleza del adsorbato. Por ejemplo, la adsorción de CO₂ en una zeolita RHO de relación Si/Al cercana a 5, induce un cambio de fase a alrededor de 2 bar, mientras que el CH₄ no tiene este efecto. Esta peculiaridad confiere a la zeolita RHO una selectividad CO₂/CH₄ muy alta en esta separación de gases [2]. La isoterma de adsorción de Ar de la zeolita ZSM-11 puramente silíceas (Silicalita-2, estructura MEL) muestra un aumento abrupto a $P/P_0=0.002$ que, mediante estudios de simulación molecular se han atribuido a modificaciones estructurales de la simetría tetragonal de la estructura MEL [5].

En este trabajo, se han estudiado los cambios estructurales de la zeolita Silicalita-2 durante la adsorción de hidrocarburos ligeros mediante técnicas de difracción de rayos X in-situ, comparándolas con sus isotermas de adsorción.

Experimental

La síntesis de Silicalita-2 se llevó a cabo siguiendo procedimientos descritos previamente [6]. La zeolita calcinada se desgasificó a 773 K y vacío durante 12 horas antes de las adsorciones. Se midieron isothermas de adsorción de Ar a 77, 87, 92 y 97 K en un ASAP-2020 (Micromeritics) equipado con un accesorio Cryotune (3P analytics) para controlar la temperatura entre 77 y 300 K. Las isothermas de adsorción de hidrocarburos se midieron utilizando un instrumento BELSORP Max-II. La muestra de Silicalita-2 se calcinó in-situ en atmósfera inerte a 873 K (8 h) y posteriormente se enfrió a temperatura ambiente en una cámara de reacción Anton-Paar XRK-900 conectada a un difractómetro de rayos X Empyrean. A continuación, se pasaron mezclas de hidrocarburo y helio en diferentes proporciones mientras se registraban los difractogramas de rayos X (DRX).

Resultados

Las isothermas de adsorción de Ar obtenidas a diferentes temperaturas se muestran en la Figura 1a. En ella, se observa un salto pronunciado en las isothermas que se desplaza hacia presiones más altas al aumentar la temperatura. Al representar las isothermas en función de la presión relativa de Ar, el salto aparece en los mismos valores de P/P_0 . Los intentos de ajustar las isothermas de Ar mediante diferentes modelos no tuvieron éxito y no se pudo calcular el calor de adsorción en todo el rango de recubrimiento. El calor de adsorción calculado en el intervalo de adsorción antes del salto en las isothermas (por debajo de 3 mmol/g) da alrededor de 12 kJ/mol, que es del orden de los valores reportados para Ar adsorbido en superficies no polares.

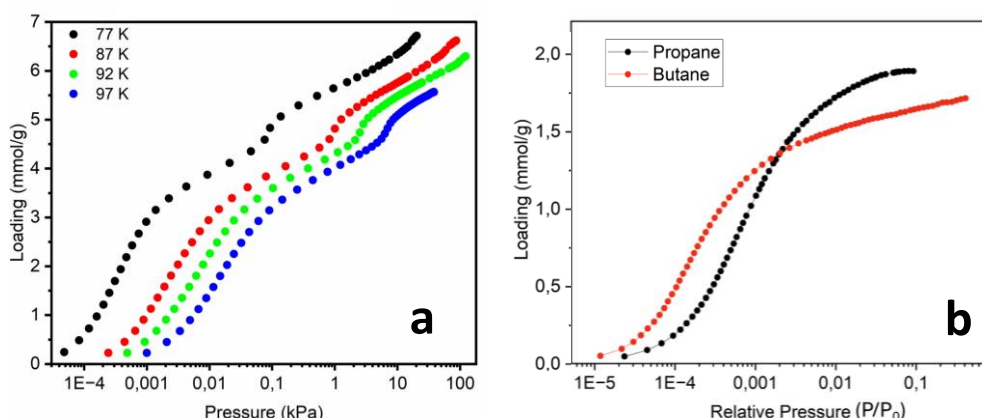


Figura 1. Isothermas de adsorción de Ar a distintas temperaturas (a), y de propano y butano a 298 K (b) en Silicalita-2.

En la Figura 1b se muestran las isothermas de adsorción de propano y butano en Silicalita-2 a 298 K. A diferencia de las de Ar, no se observa ningún cambio brusco en ellas, lo que sugiere que no hay cambio de fase. Para evaluar esta hipótesis, se realizó el estudio

estructural in-situ sometiendo la muestra a diferentes presiones parciales de hidrocarburo mientras se registraban los DRX. Todos los difractogramas medidos a diferentes presiones de propano y de butano se pudieron indexar en la misma simetría tetragonal $I-4m2$, lo que confirma que no hay cambio de fase durante la adsorción. Sin embargo, se observa un aumento del volumen de la celda unidad con la adsorción, lo que indica claramente que la estructura de la zeolita muestra una flexibilidad importante a medida que su volumen de poro se llena con el hidrocarburo, pero manteniendo su simetría.

Conclusiones

Aunque la mayoría de ejemplos de flexibilidad en zeolitas suceden por cambios de fase, en la zeolita Silicalita-2 no hay cambio de simetría, sino un aumento continuo del volumen de celda unidad, lo que sugiere una expansión elástica de la estructura debida a la presión ejercida sobre las paredes de los poros zeolíticos.

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P24. NANOCOMPOSITE MOF@CNT MODIFICADO CON PLASMAS FRÍOS PARA SU APLICACIÓN EN ELECTROCATÁLISIS

Nadia Abarchán-Mesa, Víctor K. Abdelkader-Fernández, Manuel Pérez-Mendoza*

Departamento de Química Inorgánica. Facultad de Ciencias. Universidad de Granada.

* mjperez@ugr.es

La sinergia presente en materiales híbridos que combinan las propiedades de los MOFs (elevada porosidad ajustable y presencia de centros potencialmente activos para la adsorción y catálisis) con las de nanomateriales de carbono (elevada estabilidad estructural y propiedades electrónicas sobresalientes) puede ofrecer alternativas interesantes para los retos que presentan las reacciones catalíticas claves para la producción de energía limpia, como la OER (Oxygen Evolution Reaction). El presente trabajo presenta el desarrollo de la síntesis de un nanocomposite, MOF@CNT, combinando el MOF CoFe-ZIF con nanotubos de carbono de pared múltiple funcionalizados con grupos carboxílicos (COOH-), y el estudio de su actividad como electrocatalizador en la OER. Una de las partes fundamentales del trabajo es el empleo de plasmas fríos para la modificación superficial del nanocomposite. El objetivo es estudiar si es posible mejorar la respuesta del material compuesto en la catálisis de la mencionada reacción de evolución de oxígeno.

Introducción

En el marco actual de búsqueda de alternativas que puedan contribuir al cambio del modelo energético hacia fuentes de energía más limpia, los procesos basados en la electrolisis de agua para la producción de hidrógeno verde aparecen como una de las posibilidades más viables. El efectivo desarrollo de estos procedimientos a gran escala de una manera económicamente viable requiere del desarrollo de nuevos materiales que puedan actuar de catalizadores mejorando la eficiencia de los procesos. Es especialmente clave que sean capaces de disminuir el sobrepotencial de oxígeno en la OER, y que no sean materiales excesivamente costosos o escasos, como los metales nobles que se han estudiado hasta ahora.

En este sentido, este trabajo pretende estudiar el uso de catalizadores basados en MOFs (en concreto, en el CoFeZIF) modificados con nanotubos de carbono de pared múltiple, y aplicando el uso de plasmas fríos de oxígeno e hidrógeno para modificar superficialmente los nanocomposites sintetizados. Los materiales preparados se testarán como catalizadores usando la OER como reacción de referencia que pueda darnos una idea de la capacidad que este tipo de materiales pueden tener como electrocatalizadores en procesos de generación de energía limpia.

Experimental

La síntesis del MOF CoFeZIF se ha realizado de acuerdo con lo descrito en bibliografía [1]. La obtención de los materiales híbridos se ha llevado a cabo usando nanotubos multipared (MWCNTs) funcionalizados con grupos carboxílicos y siguiendo el método de crecimiento *in-situ*. Los tratamientos con plasmas fríos se llevaron a cabo mediante un equipo de laboratorio DIENER modelo PICO equipado con una fuente de radiofrecuencia y una cámara especialmente diseñada para la homogeneización de las condiciones del plasma, usando hidrógeno y oxígeno como gases precursores. Todas las muestras preparadas se caracterizaron mediante XPS, FTIR y XRD. La actividad electrocatalítica se estudió mediante voltametría lineal de barrido (LVS), con KOH 0.1 M como electrolito.

Resultados y Conclusiones

Seguendo los procedimientos anteriormente descritos, se estudiaron cuatro muestras: CoFeZIF, CoFeZIF-CNT, CoFeZIF-CNT-pO₂ y CoFeZIF-CNT-pH₂. Las muestras corresponden a la muestra de partida, el híbrido con nanotubos de carbono y las correspondientes modificaciones con plasmas de oxígeno e hidrógeno, respectivamente. Los materiales híbridos mostraron mejores propiedades electrocatalíticas que los materiales de partida por separado, y los tratamientos con plasmas se muestran efectivos a la hora de mejorar el comportamiento como catalizadores de estos materiales en la OER. Los datos de caracterización permiten relacionar las modificaciones superficiales introducidas mediante el tratamiento con los plasmas con el incremento en la actividad catalítica, debido a la generación de defectos y nuevos sitios que actúan como centros activos accesibles para que se facilite la reacción.

Agradecimientos

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P25. Polyamine-Based Enhancer for Improved Scale Inhibitor Retention in Sandstone

Rafael T. Landim¹, Artur V. Nascimento¹, Pedro B. Cavalcante¹, Célio L. Cavalcante Jr.¹, F. Murilo T. Luna^{1*}.

¹Universidade Federal do Ceará, Departamento de Engenharia Química, Grupo de Pesquisa em Separações por Adsorção, Campus do Pici, Bl. 709, Fortaleza, CE, Brazil.

*Corresponding author: murilo@ufc.br

ABSTRACT

Inorganic scale deposition in oil reservoirs reduces productivity and increases operational costs, making the retention of phosphonate-based scale inhibitor (SI) an important factor for effective scale control. In this study was evaluated a polyamine-based as a retention enhancer for a commercial SI in sandstone through batch and fixed-bed column experiments. Batch experiments showed that polymer addition increased SI retention by up to 69% at a concentration of 50 mg.L⁻¹. Under dynamic flow conditions, the polymer-containing system exhibited higher residual SI concentrations during the elution stage, reaching approximately 25 mg L⁻¹ compared with 10 mg L⁻¹ for the SI-only system. These results demonstrate the potential of polyamine-based enhancer to strengthen SI–rock interactions, thereby enhancing inhibitor retention and promoting a more gradual release.

INTRODUCTION

Inorganic salt scaling in oil wells reduces productivity and increases operational costs. Although phosphonate-based scale inhibitors are widely used to mitigate this problem, their effectiveness depends on retention within the porous medium, which is governed by adsorption and precipitation mechanisms influenced by rock mineralogy and system chemistry [1]. Cationic polymers have emerged as a promising alternative for enhancing SI–rock interactions due to the presence of functional groups capable of interacting simultaneously with the inhibitor and the mineral surface.

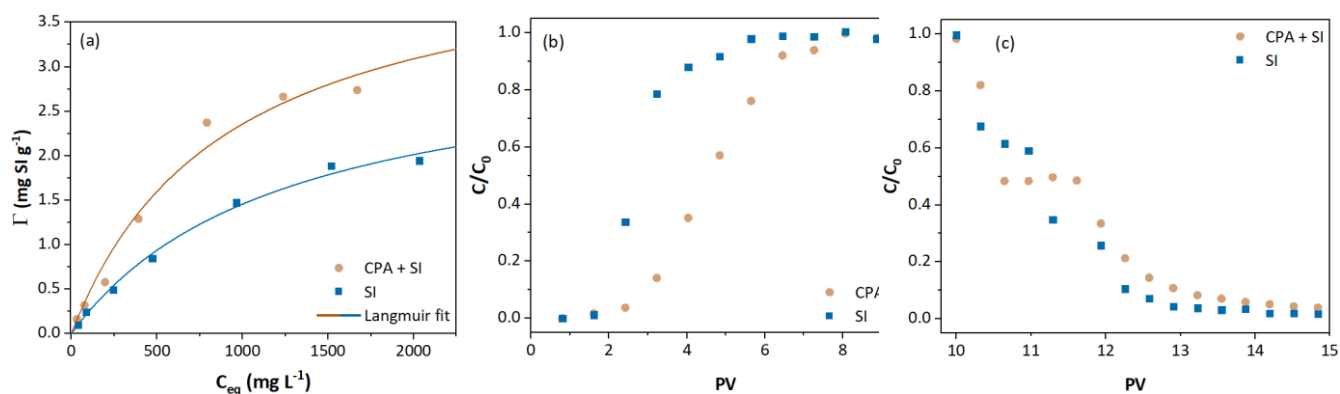
In this context, the retention of a commercial SI was evaluated in a sandstone sample in the absence and presence of a polyamine-based enhancer. Batch retention and fixed-bed experiments were performed to assess both the equilibrium and the dynamic behavior of the system, providing a preliminary evaluation of the polymer's ability to enhance SI retention.

EXPERIMENTAL SECTION

A sandstone sample, a commercial SI based on diethylenetriamine pentamethylene phosphonic acid (DETPMP), and a water-soluble cationic polyamine (CPA, Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine)) were used throughout the experiments. Batch retention experiments were carried out using 4.0 g of sandstone (150–300 μm) and 0.1 L of a 50:50 (v/v) mixture of SI (50–2,000 mg L^{-1} , pH 4) and polyamine-based polymer (4,000 mg L^{-1}) solutions. An experiment containing only the SI was also conducted. All solutions were prepared in 2 wt.% KCl and maintained at 70°C under constant stirring for 120 min. The retained SI amount was determined by mass balance, and the equilibrium data were fitted to the Langmuir equation to estimate the maximum retention capacity. Fixed-bed experiments were performed using a stainless-steel column (0.95 cm internal diameter, 25 cm length, and 17.72 cm^3 volume) packed with crushed sandstone (300–500 μm). The SI solution (500 mg L^{-1} , pH 4.0) and the polymer solution (4,000 mg L^{-1}) were prepared in KCl (2% wt.). The polymer was injected first, followed by the SI solution, both at a flow rate of 0.5 mL min^{-1} . After a 16 h shut-in period at 70°C, the flow was continued with KCl (2% wt.) at 0.2 mL min^{-1} , without SI or polymer addition. For both batch and fixed-bed experiments, the phosphorus concentration in the collected samples was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

RESULTS AND DISCUSSION

The addition of the polymer increased inhibitor retention at all evaluated concentrations, with improvements ranging from 18% to 69%, the highest gain being observed at 50 mg L^{-1} (see Figure 1a). Furthermore, using the parameters estimated from the Langmuir equation, the maximum retention capacity for the studied system



increased from 3.26 to 4.48 mg g^{-1} .

Figure 1 - Retention of the scale inhibitor (SI) with and without the presence of the polymer: (a) batch retention isotherms, (b) concentration profiles during the retention step, and (c) elution profiles under dynamic flow conditions.

The retention profiles obtained from the fixed-bed experiments demonstrated that the presence of the polymer enhanced SI retention within the porous medium (Figure 1b). While the system containing only SI reached saturation after approximately 5.5 pore volumes (PV), the CPA + SI system approached saturation only after 8.0 PV, indicating a delayed inhibitor transport front. During the elution stage, the polymer-containing system consistently exhibited higher residual inhibitor concentrations than the SI-only system, particularly at low concentration levels (Figure 1c). At approximately 14 PV, the SI-only system showed a concentration of about 10 mg L^{-1} , whereas the CPA + SI system maintained approximately 25 mg L^{-1} , corresponding to a 150% higher residual concentration.

CONCLUSIONS

The polyamine-based sample enhanced SI retention in sandstone. In batch experiments, retention improvements of up to 69% were observed, while under flow conditions, delayed SI transport and higher residual concentrations were detected during the elution stage. These results highlight the potential of polymer addition to strengthen SI-rock interactions, thereby enhancing retention and promoting a more gradual release within the porous medium.

Acknowledgments

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P26. Reduction of ammonia emissions and nutrient recovery through adsorption in livestock facilities

Jana Sanz, Alejandro Lete, Noemí Gil-Lalaguna, Ángela Millera, Jesús Ceamanos, Isabel Fonts*, Gloria Gea

Thermochemical Processes Group (I3A), Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain

isabelfo@unizar.es

Abstract

The gas-phase adsorption of ammonia (NH_3) on porous carbonaceous materials obtained through three different methods—pyrolysis, chemical activation with oxoacids followed by pyrolysis, and pyrolysis followed by chemical activation with oxoacids—has been studied experimentally. It was found that the NH_3 adsorption capacity increases outstandingly only when chemical activation takes place after pyrolysis, reaching values around 400 mg/g. The effect of the presence of moisture in the gas atmosphere during NH_3 adsorption over the best adsorbent was evaluated, and it was found that the presence of moisture decreases the NH_3 adsorption capacity by half.

Introduction

Ammonia (NH_3) emissions represent a major environmental concern due to their role in particulate matter formation and their contribution to ecosystem acidification and eutrophication. Agricultural activities are the dominant source of these emissions, with livestock manure management accounting for a significant fraction. This situation has stimulated growing interest in the development of sustainable adsorbent materials capable of mitigating NH_3 release into the atmosphere. The treatments currently promoted as the best available techniques (BAT) for controlling ammonia emissions, such as absorption in acidic solutions or biofilters (after air-stripping of the manure), have drawbacks, including technical complexity, low concentrations of recovered ammonium salts in the solution, and the generation of nitrous oxide; these issues could be addressed by adsorption on porous carbonaceous solids. Furthermore, adsorption could allow this nutrient to be recovered in a form suitable for use as fertilizer in agriculture, thereby not only preventing NH_3 emissions but also achieving its valorization.

The ammonia molecule has a small kinetic diameter, high polarity, and a strongly basic character; therefore, it is expected that, to maximize its adsorption, the presence of ultra- and micropores is necessary, in addition to functional groups that promote its adsorption through chemical interactions. In this regard, this study will examine how the activated carbon preparation process (pyrolysis temperature and chemical activation

before or after pyrolysis) affects the adsorption capacity of NH_3 in single-bed adsorption tests. In order to produce a solid material that can be used as fertilizer, sulfuric acid will be used for activation, and the formation of ammonium sulfate on the surface of the biochar during adsorption will be evaluated. Lastly, given that the atmosphere containing NH_3 may also contain a significant percentage of moisture, the competitive adsorption of ammonia and moisture will be studied using the solid that has demonstrated the greatest NH_3 adsorption capacity.

Experimental

With the aim of studying the influence of the activation methodology, three methodologies were followed. In the first one, the rice husk was directly pyrolyzed at 350 or 750 °C (RH_350 and RH_750), in the second one rice husk was impregnated with the activating agent prior to pyrolysis (RH_H₂SO₄_350 and RH_H₂SO₄_750), whereas in the third one, biochar was initially obtained and subsequently impregnated (RH_350_H₂SO₄ and RH_750_H₂SO₄). In both methodologies, H₂SO₄ was employed as an activating agent at a concentration of 40% (w/w). In the second methodology, rice husk was directly impregnated with a solution of the activating agent (liquid/solid ratio 20 mL·g⁻¹) for 6 h under stirring at room temperature. In the third one, the rice husk underwent pyrolysis, and the biochar obtained was impregnated with the activating agent (14 mL·g⁻¹) for 4 h under stirring, followed by a contact time of 24 h without stirring. In both cases, after impregnation, the solids were filtered and dried.

The NH_3 adsorption tests were performed in a fixed-bed device continuously fed with either a gas stream of 1000 ppm NH_3 in Ar or a gas stream of 1000 ppm NH_3 and 4500 ppm of H₂O in Ar, in order to analyze the influence of the presence of moisture on the NH_3 adsorption process. The procedure and concentration values were chosen to be representative of the conditions in a livestock facility. The outlet concentration was monitored by Micro GC, allowing the determination of the breakthrough curve. By applying a non-steady-state material balance to this curve, the adsorption capacity of each material was calculated, expressed in mg NH_3 g⁻¹ of adsorbent.

Results

The results in Table 1 show that the pristine solid derived from the pyrolysis of rice husks, as well as that derived from the activation of the husks with sulfuric acid prior to pyrolysis, have very low ammonia adsorption capacities (< 10 mg g⁻¹). However, activation with sulfuric acid following pyrolysis treatment yields adsorbents with an NH_3 adsorption capacity of around 400 mg g⁻¹, which corresponds to a concentration of the nutrients approximately 100 times higher than its concentration in the pig manure.

However, under conditions more realistic to those of a stream from air stripping, the capacity of this adsorbent, while still high (200 mg g^{-1}), is reduced by half due to the reduction of the acid character of the biochar surface. Ammonium salts $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$ were detected in the adsorbent surface after adsorption.

Table 1-. NH_3 adsorption capacity for the different activated carbons produced.

	RH_350	RH_750	RH_H2SO4_350	RH_H2SO4_750	RH_350_H2SO4	RH_750_H2SO4	RH_750_H2SO4
				0		4	
$C_{\text{ads},\text{NH}_3} (\text{mg} \cdot \text{g}^{-1})$	7.5	3.8	12	1	250	400	200

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P27. Optical Activation versus Function in Phenolic Interfacial Charge-Transfer Complexes of Tetragonal ZrO₂: A Combined Experimental and DFT Study

Miljana Dukić^{1*}, Katarina Isaković¹, Valentina Nikšić¹, Dušan Sredojević¹, Hristina Šalipur², Davor Lončarević², Miriama Malček-Šimunkova³, Joaquín Silvestre-Albero⁴, Anđela Rajčić¹, Jovana Periša¹, Vesna Lazić¹

¹*Vinča Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade, Centre of Excellence for Photoconversion, P.O. Box 522, 11001 Belgrade, Serbia*

²*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of Republic of Serbia, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia*

³*Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

⁴*Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, San Vicente del Raspeig 03690, Spain*

**miljana.dukic@vin.bg.ac.rs*

Summary

Surface functionalization of metal-oxide nanoparticles with phenolic ligands forms interfacial charge-transfer (ICT) complexes that extend visible-light absorption, and is widely assumed to improve photocatalytic performance. We test that assumption on a single, phase-pure tetragonal ZrO₂ platform modified with salicylic acid, 3,5-di-tert-butylsalicylic acid, catechol, and caffeic acid, combining XRD, UV-Vis, BET, FTIR, and EPR with density functional theory cluster calculations. All ligands introduced ligand-to-metal charge transfer and a systematic narrowing of the optical gap, with Kubelka-Munk values in close quantitative agreement with the calculated spectra. However, this optical activation did not enhance function: unmodified t-ZrO₂ gave the highest hydrogen evolution and the strongest hydroxyl-radical EPR signal, while ligand grafting generally suppressed both. Visible-light activation and photocatalytic performance are thus decoupled in this system.

Introduction

Zirconium dioxide (ZrO₂) is a chemically and thermally robust wide-bandgap semiconductor, but its photocatalytic activity is intrinsically restricted to the UV region. One established strategy for extending its response into the visible range is surface functionalization with phenolic ligands, which form interfacial charge-transfer (ICT) complexes via ligand-to-metal charge transfer (LMCT) from the bound organic molecule to the ZrO₂ conduction band. The optical consequences of ICT formation are well

documented; however, the literature assessing whether visible-light activation improves photocatalytic function intrinsically remains scarce. Phenolic ligands differing in anchoring geometry and redox behavior may narrow the optical gap, yet simultaneously alter surface-active sites and reactive-oxygen-species (ROS) generation in ways that are not necessarily beneficial. The aim of this work was to disentangle optical activation from photocatalytic function in a single, phase-pure tetragonal ZrO_2 platform, by combining experimental characterization with density functional theory (DFT) for a series of phenolic ICT complexes.

Experimental

Phase-pure tetragonal ZrO_2 was prepared hydrothermally and functionalized afterward with SA, DTBSA, CAT, and CA by surface coordination. Materials were characterized by XRD, N_2 physisorption (BET, pore-size distribution), UV-Vis diffuse reflectance (Kubelka-Munk), and FTIR; surface radicals were probed by EPR spin trapping with DMPO under *in situ* excitation at 365 nm. Optical and electronic properties were modeled by DFT on the $[\text{Zr}_{10}\text{O}_{16}(\text{OH})_6]$ cluster. Photocatalytic hydrogen evolution was evaluated in aqueous suspensions (125 mg catalyst in 250 cm^3 water) containing 2-propanol as a sacrificial agent and *in situ* photodeposited Pt (0.5 wt%) as a cocatalyst, under irradiation from a 100 W mercury lamp, with evolved H_2 quantified by gas chromatography (TCD).

Results and Discussion

XRD confirmed a phase-pure tetragonal ZrO_2 support, with the characteristic (101) reflection at $2\theta \approx 30.2^\circ$ and no detectable monoclinic contribution; N_2 physisorption gave a mesoporous solid ($S_{\text{BET}} \approx 117 \text{ m}^2 \text{ g}^{-1}$, mean pore diameter $\approx 6 \text{ nm}$). Surface modification produced a pronounced redshift of the absorption edge for all ligands, and the Kubelka-Munk optical gaps decreased systematically ($\text{SA} > \text{DTBSA} > \text{CA} > \text{CAT}$), in close quantitative agreement with the DFT-calculated values. This confirms the LMCT character of the new visible-region absorption: in the calculated electronic structure, the HOMO is localized on the ligand and the conduction-band minimum on the ZrO_2 cluster. In photocatalytic hydrogen evolution, unmodified t- ZrO_2 was the most active catalyst, substantially outperforming all ICT complexes; among the modified samples, only t- ZrO_2/CA reached comparable rates, and only after an induction period associated with *in situ* Pt photodeposition. The remaining ligands (SA, DTBSA, CAT) gave consistently low H_2 production. EPR spin trapping under 365 nm irradiation produced the characteristic •DMPO-OH adduct ($a_{\text{N}} = 1.503 \text{ mT}$, $a_{\text{H}\beta} = 1.477 \text{ mT}$, $g = 2.0059$) for all samples. Unmodified t- ZrO_2 showed the highest integrated •OH intensity, with ligand-modified samples giving lower yields, consistent with steric shielding (DTBSA) and radical scavenging (SA, CA). For the CA system, additional •DMPO-OOH (superoxide) and a secondary adduct were resolved, indicating a distinct ROS profile rather than a higher overall radical flux. This concordance between the photocatalytic and EPR results

indicates that the limiting factor is not visible-light harvesting but the utilization of photogenerated charge carriers at the modified surface, where the bound ligands act as recombination or scavenging sites rather than productive electron donors. Taken together, these results show that on phase-pure t-ZrO₂, the optical signature of ICT formation is decoupled from photocatalytic function: ligand grafting reliably extends visible-light absorption, but does not enhance, and in most cases suppresses, the photocatalytic and radical-generating performance relative to the unmodified oxide.

Conclusions

Phenolic surface modification of phase-pure tetragonal ZrO₂ generates ICT complexes whose LMCT character and systematic gap narrowing are confirmed by the quantitative agreement between Kubelka-Munk and DFT optical gaps, so visible-light activation is robust and predictable. This activation, however, does not translate into improved H₂ evolution or radical generation: unmodified t-ZrO₂ remained the most active material, while phenolic ligands generally lowered both H₂ production and •OH yield, consistent with steric blocking and radical scavenging. These findings caution against using a redshifted absorption edge as a proxy for photocatalytic performance, and show that interface design must optimize charge utilization at the surface, not merely light harvesting.

Acknowledgments

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P28. Surgical Mask-Derived Activated Carbons for Heavy-Metal Adsorption

Paula Ramos Cayero, Eduardo M. Cuerda Correa, Carmen Fernández-González, María F. Alexandre Franco*

Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Avenida de Elvas s/n, 06006, Badajoz, España.

* *malexandre@unex.es*

The conversion of plastic waste into adsorbent materials represents a promising strategy for combining waste valorisation with water decontamination. In this work, discarded surgical masks were evaluated as precursors of carbonaceous adsorbents for the removal of Zn(II), Cd(II), and Pb(II) from aqueous solution. Surgical masks were first treated with concentrated H₂SO₄ and subsequently subjected to physical activation with steam at 800 °C. Steam activation caused a dramatic development of porosity, increasing the BET surface area from 0.88 to 632 m² g⁻¹, while also producing major changes in surface chemistry and the point of zero charge. Both materials showed the ability to retain the three metal ions, and the adsorption kinetics were satisfactorily described by the pseudo-second-order model. Interestingly, the large difference in surface area between the two adsorbents did not lead to proportional differences in metal uptake, indicating that adsorption was controlled by the combined effects of porosity, surface chemistry, and accessibility of active sites. These results demonstrate the potential of discarded surgical masks as precursors of carbonaceous adsorbents for aqueous-phase remediation.

Introduction

The increasing generation of single-use plastic waste has encouraged the development of strategies for converting polymeric residues into value-added materials. Disposable surgical masks, composed mainly of polypropylene and containing very little mineral matter, are potentially attractive precursors for the preparation of carbonaceous adsorbents. However, the thermoplastic nature of these materials makes their conversion into porous carbons challenging and requires suitable pretreatment and activation procedures.

In this work, surgical masks were converted into carbonaceous adsorbents by sulfuric-acid treatment followed by steam activation. The resulting materials were characterized in terms of porous texture and surface chemistry and evaluated for the adsorption of Zn(II), Cd(II), and Pb(II) from aqueous solution.

Experimental

Surgical masks were stripped of metallic components and elastic straps, cut into small pieces, and used as carbonaceous precursors. The starting material contained 85.72 wt.% carbon and negligible ash content. The first adsorbent, MS, was prepared by treating 15 g of mask material with 300 mL of 12 M H_2SO_4 under heating. After evaporation of the liquid phase, the solid was washed to approximately neutral pH and dried. A fraction of MS was subsequently activated with steam at 800 °C for 1 h, yielding the material MV. The adsorbents were characterized by elemental analysis, SEM, N_2 adsorption at -196 °C, mercury intrusion porosimetry, FTIR spectroscopy, Boehm titration, and pH_{PZC} determination. Adsorption kinetics were studied at 30 °C using approximately 0.1 g of adsorbent and 20 mL of individual Zn(II), Cd(II), or Pb(II) solutions. Residual metal concentrations were determined by atomic absorption spectrometry.

Results and discussion

Sulfuric-acid treatment produced the MS material with a high yield of 97.87%, but with negligible porosity. Its BET surface area was below $1 \text{ m}^2 \text{ g}^{-1}$, with micropore and mesopore volumes of 0.0002 and $0.0015 \text{ cm}^3 \text{ g}^{-1}$, respectively. Nevertheless, the treatment strongly modified the surface chemistry, generating predominantly acidic functionalities and a pH_{PZC} of 1.96. Steam activation markedly changed both the porous structure and the surface properties. The resulting MV material showed a BET surface area of $632 \text{ m}^2 \text{ g}^{-1}$, together with micropore and mesopore volumes of 0.25 and $0.11 \text{ cm}^3 \text{ g}^{-1}$, respectively. Its pH_{PZC} increased to 9.25, indicating a substantial shift toward a more basic surface character. Both materials removed Zn(II), Cd(II), and Pb(II) from aqueous solution, as can be seen in Figure 1.

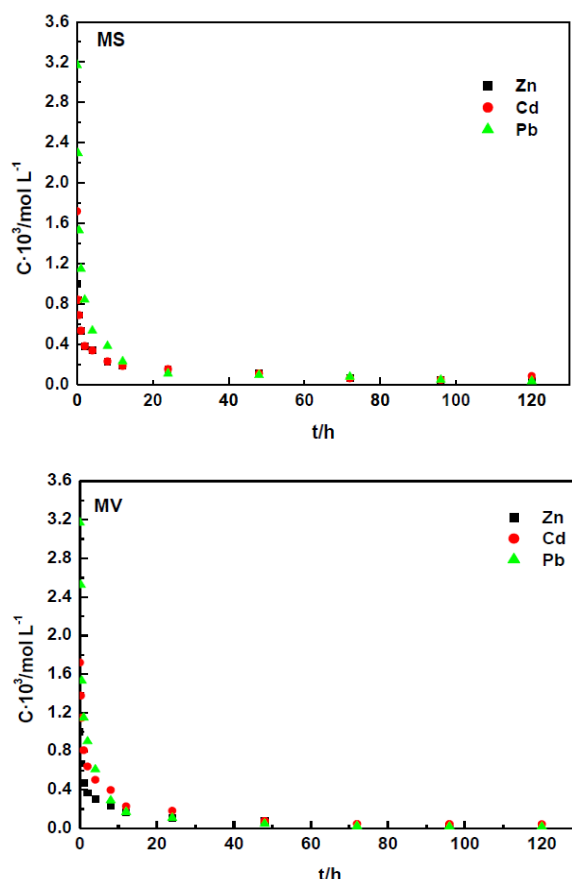


Figure 1- Adsorption kinetics of Zn(II), Cd(II), and Pb(II) by samples MS (left) and MV (right).

Adsorption increased progressively with contact time, and the kinetic data were satisfactorily described by the pseudo-second-order model. These results indicate a strong dependence of the overall adsorption rate on the concentration of available adsorption sites, although kinetic-model fitting alone should not be interpreted as direct evidence of a unique adsorption mechanism. Interestingly, the large difference in surface area between MS and MV did not produce proportionally different metal uptakes. This indicates that adsorption was not governed exclusively by porosity, but also by surface functionality, acid-base properties, and accessibility of active sites. Thus, steam activation was decisive for pore development, whereas surface chemistry remained a key factor controlling metal-ion adsorption.

Conclusions

Discarded surgical masks were converted into carbonaceous adsorbents by sulfuric-acid treatment followed by steam activation. The acid-treated material was strongly acidic but almost nonporous, whereas activation at 800 °C increased the BET surface area from below 1 to 632 m² g⁻¹ and shifted the pHPZC from 1.96 to 9.25. Both materials adsorbed Zn(II), Cd(II), and Pb(II), with kinetics well described by the pseudo-second-order model.

The limited effect of the large surface-area increase on metal uptake indicates that adsorption depends not only on porosity, but also on surface chemistry and site accessibility.

P29. Optimizing Methylene Blue Biosorption with Alginate Beads

Manuel Merino Gallardo, Carmen Fernández-González, Eduardo M. Cuerda Correa,
María F. Alexandre Franco*

Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Avenida de Elvas s/n, 06006, Badajoz, España.

* *malexandre@unex.es*

Methylene blue removal from aqueous solution by biosorption onto calcium alginate beads was investigated and optimized using response surface methodology. A three-factor central composite design was applied to evaluate the effects of temperature, stirring rate, and sodium alginate concentration on removal efficiency and the specific adsorption rate constant. Temperature and alginate concentration were the dominant variables, but their effects on the two responses were opposite: dye removal was favored by lower temperature and higher alginate concentration, whereas adsorption kinetics improved at higher temperature and lower alginate concentration. The quadratic models explained 94.81% and 96.37% of the variability in removal efficiency and rate constant, respectively. Simultaneous optimization predicted 9.6 °C, 286 rpm, and 3.3% alginate as the best compromise. Experimental validation yielded 89.6% removal and a specific rate constant of 0.0946 min⁻¹, confirming the usefulness of multi-response optimization for alginate-based biosorption.

Introduction

Synthetic dyes are persistent water pollutants whose complex molecular structures often make them resistant to conventional biological treatment. Biosorption offers a low-cost alternative based on materials of biological origin. Alginate is particularly attractive because it readily forms stable calcium-crosslinked hydrogels containing carboxylate-rich binding domains. In this work, calcium alginate beads were formed in situ in the presence of methylene blue. A statistical design of experiments was used to quantify the effects of temperature, stirring rate, and alginate concentration on both dye removal efficiency and adsorption kinetics, and to identify a compromise operating region through simultaneous multi-response optimization.

Experimental

Calcium alginate beads were produced by dropwise addition of sodium alginate solution to a methylene-blue solution containing CaCl₂, so that ionic gelation and dye biosorption occurred simultaneously. Residual methylene blue was quantified by UV-Vis spectrophotometry at 664 nm. A 23-run central composite design was used. Temperature, stirring rate, and sodium alginate concentration were varied over 10–40

°C, 60–340 rpm, and 0.01–2.0%, respectively. The response variables were removal efficiency and the specific adsorption rate constant, k_a . Data were analyzed by ANOVA and quadratic regression, followed by Pareto, main-effect, interaction, and response-surface analyses. A desirability function was finally used for simultaneous optimization of both responses.

Results and discussion

Preliminary experiments showed that temperature and alginate concentration strongly affected both responses, whereas stirring rate had a smaller individual effect. Removal efficiency decreased as temperature increased, consistent with an overall exothermic biosorption process, while increasing alginate concentration enhanced dye removal by increasing the amount of available biosorbent. The kinetic response followed the opposite trend: the specific rate constant increased with temperature and generally decreased as alginate concentration increased. The statistical models described the experimental data satisfactorily. The quadratic model for removal efficiency explained 94.81% of the observed variability, while the corresponding model for the specific rate constant explained 96.37%. ANOVA confirmed temperature and alginate concentration as the principal statistically significant variables. Interaction terms were also relevant, demonstrating the advantage of a multivariable design over a one-factor-at-a-time strategy. The opposite influence of the main variables created a clear optimization trade-off. Conditions favouring maximum removal were not those producing the fastest adsorption. Individual optimization of removal efficiency predicted 95% removal at 7 °C, 220 rpm, and 2.52% alginate; experimental validation gave 88.9%. Because this optimum lay partly outside the original design domain, the result was interpreted with the expected caution associated with extrapolation. A desirability function (Figure 1) was therefore applied to obtain a practical compromise between high dye removal and rapid adsorption. The simultaneous optimum was predicted at 9.6 °C, 286 rpm, and 3.3% alginate. Under these conditions, the model predicted 100% removal and $k_a = 0.102 \text{ min}^{-1}$. Experimental validation yielded 89.6% removal and $k_a = 0.0946 \text{ min}^{-1}$, showing good agreement for the kinetic response and confirming the usefulness of the optimization strategy.

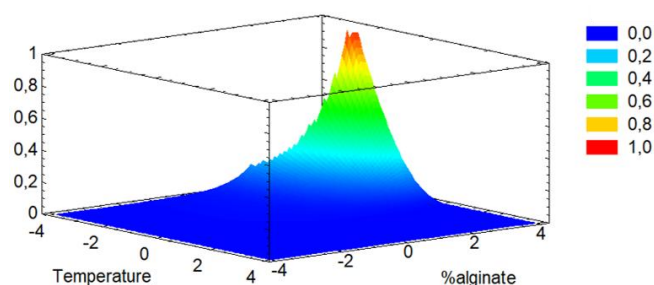


Figure 1- Response surface plot of the desirability function as a function of temperature and alginate concentration.

These results show that multi-response optimization provides a more realistic basis for biosorption process development than maximizing removal percentage alone. The antagonistic effect of temperature and alginate concentration on efficiency and kinetics makes statistical optimization particularly valuable when process productivity and treatment performance must be considered simultaneously.

Conclusions

Calcium alginate beads effectively removed methylene blue from aqueous solution. Response surface methodology identified temperature and alginate concentration as the main factors controlling the process, with opposite effects on removal efficiency and adsorption kinetics. Simultaneous optimization provided a practical compromise, experimentally yielding 89.6% dye removal and $k_a = 0.0946 \text{ min}^{-1}$. The study demonstrates that statistical experimental design is a useful tool for optimizing alginate-based biosorption processes when multiple performance criteria must be balanced.

P30. Textural Control and ANN Modelling of CaO-Based Sorbents for CO₂ Capture

Alberto J. Nieto-Sánchez, María F. Alexandre-Franco, Eduardo M. Cuerda-Correa*

Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Avenida de Elvas s/n, 06006, Badajoz, España.

* emcc@unex.es

CaO-based sorbents were prepared from synthetic CaCO₃ precursors whose texture was tailored through a 23-run central composite design. Synthesis temperature, stirring rate, and Triton X-100 percentage were evaluated by response surface methodology (RSM), while CO₂ capture was modelled through multiple regression and artificial neural networks (ANNs). An optimized precursor with a BET surface area of 116 m² g⁻¹ was obtained. The textural parameter controlling uptake depended strongly on CO₂ partial pressure: surface area and microporosity were most relevant under diluted CO₂, whereas mesoporosity became dominant in pure CO₂. A ten-neuron ANN reproduced uptake data with R = 0.99 within the experimental domain. Cycling tests further showed that appropriate synthesis conditions can limit pore shrinkage: one sorbent retained 92.6% of its initial capture capacity after 11 carbonation-calcination cycles. The results demonstrate the value of combining textural engineering, RSM, and ANN modelling for CaO sorbent design.

Introduction

Calcium looping is a promising high-temperature route for post-combustion CO₂ capture, but the practical use of CaO-based sorbents is limited by progressive sintering and loss of reactive surface during repeated carbonation-calcination cycles. Synthetic CaCO₃ precursors offer an opportunity to control crystal habit, surface area, and pore architecture before conversion to CaO. In this work, the effects of synthesis temperature (ST), stirring rate (SR), and surfactant percentage (SP) on the texture and CO₂ capture performance of CaO-derived sorbents were investigated. A factorial central composite orthogonal and rotatable design, response surface methodology, multiple regression, and artificial neural networks were combined to identify synthesis-property-performance relationships under pure and diluted CO₂ streams.

Experimental

Synthetic CaCO₃ was precipitated from 0.1 M CaCl₂ and Na₂CO₃ solutions in the presence of controlled amounts of Triton X-100. A 23-experiment central composite design comprised eight factorial points, six axial points, and nine centre-point replicates. ST, SR, and SP were the operating factors, while BET surface area (S_{bet}), micropore volume (V_{mi}), mesopore volume (V_{me}), total pore volume, and CO₂ uptake were the responses. The

precipitated carbonates were calcined at 950 °C for 4 h under N₂ to obtain CaO-based sorbents. CO₂ uptake was measured thermogravimetrically at 650 °C for 120 min under either pure CO₂ or 15% CO₂ in N₂. Selected sorbents were subjected to 11 consecutive carbonation-calcination cycles under diluted CO₂. Data were analysed by RSM, multivariate regression, and feedforward ANNs trained by Levenberg-Marquardt backpropagation.

Results and discussion

RSM showed that surfactant percentage was the main factor controlling S_{BET} , while significant ST×SR and ST×SP interactions confirmed that the synthesis variables could not be optimized independently. The predicted optimum, 26 °C, 329 rpm, and 0.16% Triton X-100, yielded a CaCO₃ precursor with $S_{\text{BET}}=116 \text{ m}^2 \text{ g}^{-1}$, in excellent agreement with the model. The surfactant also modified the calcite/aragonite ratio and acted as a crystal-growth modifier, whereas calcination produced partially sintered cubic CaO particles with only minor secondary phases. The 23 sorbents showed CO₂ uptakes of 43.7–98.7% in pure CO₂ and 46.2–65.0% in a 15% CO₂ stream. Regression models described both datasets with $R^2>0.95$, although the controlling textural variables depended on gas composition. Under diluted CO₂, uptake correlated mainly with S_{BET} and micropore volume, whereas mesopore volume became dominant under pure CO₂. This suggests that, at low CO₂ partial pressure, capture is favoured at accessible high-energy sites in narrow pores, while at higher pressure diffusion and reaction within wider mesopores become increasingly important.

ANN modelling confirmed the nonlinear relationship between texture and capture performance. A feedforward network using S_{BET} and V_{me} as inputs and the two CO₂ uptake values as outputs required only ten hidden neurons to achieve $R=0.99$ within the experimental domain. The model accurately reproduced the experimental responses and complemented the mechanistic interpretation provided by RSM and regression analysis.

Cycling tests (Figure 1) revealed a trade-off between initial uptake and structural stability. Most sorbents progressively lost capacity, whereas sample 13 remained nearly constant over 11 cycles, with only a 3.6 percentage-point loss. These results indicate that highly developed narrow porosity favours initial capture but is more vulnerable to sintering and pore blockage, whereas a more open structure can provide greater long-term stability.

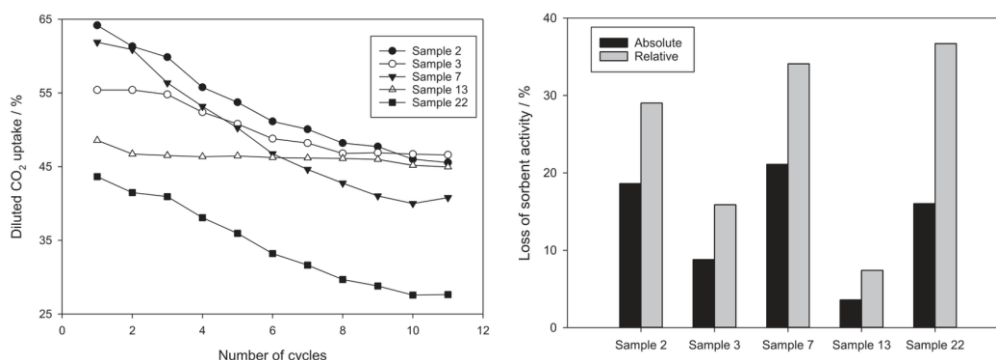


Figure 1- CO₂ uptake over 11 cycles and activity loss for selected CaO-based sorbents.

Conclusions

Textural engineering of synthetic CaCO₃ precursors effectively controls CaO-based CO₂ capture. RSM produced a precursor with $S_{\text{BET}} = 116 \text{ m}^2 \text{ g}^{-1}$ and revealed significant variable interactions. Surface area and microporosity dominated under diluted CO₂, whereas mesoporosity was more relevant in pure CO₂. ANN models accurately reproduced uptake within the experimental domain. Cycling tests showed that a more open pore structure can reduce sintering-related deactivation and sustain capture capacity.

P31. Beyond Empirical Kinetics: Intraparticle Diffusion Modelling of Paraben Adsorption

Juan Manuel Garrido Zoido, María F. Alexandre Franco, Eduardo M. Cuerda-Correa*

Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Avenida de Elvas s/n, 06006, Badajoz, España.

* emcc@unex.es

Adsorption of methyl-, ethyl-, propyl-, and butylparaben on DOWEX OPTIPORE L493 was described using a heterogeneous intraparticle diffusion model (IPDM) coupled with Langmuir equilibrium. The transient model was solved by the method of lines and fitted to batch kinetic data by nonlinear least squares, giving excellent agreement for all compounds ($R^2 = 0.9969\text{--}0.9997$). Estimated pore diffusivities were comparable in magnitude to Wilke-Chang molecular diffusivities and decreased with molecular size according to $D_p \propto V_{vdW}^{-0.53}$. Independent equilibrium analysis yielded an approximately constant monolayer capacity of 0.81 mmol g^{-1} for all four parabens. Cross-comparison of kinetic and equilibrium parameters supported the physical consistency of the model and showed the value of mechanistic diffusion modelling beyond empirical kinetic equations.

Introduction

Empirical kinetic equations are widely used in adsorption studies because of their simplicity, but they generally provide limited mechanistic insight and little predictive capability outside the experimental conditions used for fitting. In contrast, diffusion models based on mass conservation and transport laws offer a more physically meaningful description of adsorption dynamics and allow the estimation of parameters with direct phenomenological significance. In this work, a three-parameter heterogeneous intraparticle diffusion model (IPDM) was developed and validated for the adsorption of four homologous parabens on a highly porous polymeric resin. The model combines pore diffusion with Langmuir equilibrium and was fitted to transient concentration data through numerical solution of the governing equations. This approach enabled transport and equilibrium parameters to be estimated within a unified framework and subsequently compared with independently obtained equilibrium data.

Experimental

Adsorption experiments were carried out using DOWEX™ OPTIPORE™ L493, a highly cross-linked macroporous styrenic resin with a BET surface area of $1100 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $1.16 \text{ cm}^3 \text{ g}^{-1}$. Methyl-, ethyl-, propyl-, and butylparaben were used as adsorbates. Equilibrium experiments were performed at 20°C using 250 mL of aqueous

solution containing 5 mg L^{-1} of each paraben and adsorbent masses ranging from 10 to 70 mg. For kinetic experiments, 50 mg of resin were contacted with 250 mL of a 5 mg L^{-1} paraben solution at 20°C under continuous magnetic stirring for 48 h. Samples were withdrawn at selected times, and paraben concentrations were determined by UV–Vis spectrophotometry at 254 nm. The IPDM was formulated from mass balances in the fluid and particle phases, assuming spherical particles, negligible external mass-transfer resistance, pore diffusion as the controlling transport mechanism, and local equilibrium described by the Langmuir isotherm. The resulting partial differential equation was solved numerically by the method of lines, and the three model parameters were estimated by nonlinear least-squares minimization. Local sensitivity analysis was subsequently applied to determine parameter uncertainties and 95% confidence intervals.

Results and discussion

The IPDM reproduced the kinetic curves accurately (Figure 1), with R^2 values of 0.9969–0.9997. Predicted profiles showed rapid depletion near the particle surface followed by progressive penetration into the pore network, consistent with intraparticle diffusion control. Diffusion time constants were 78.8–99.0 s, while pore diffusivities of $8.2\text{--}10.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ were comparable in magnitude to Wilke–Chang molecular diffusivities.

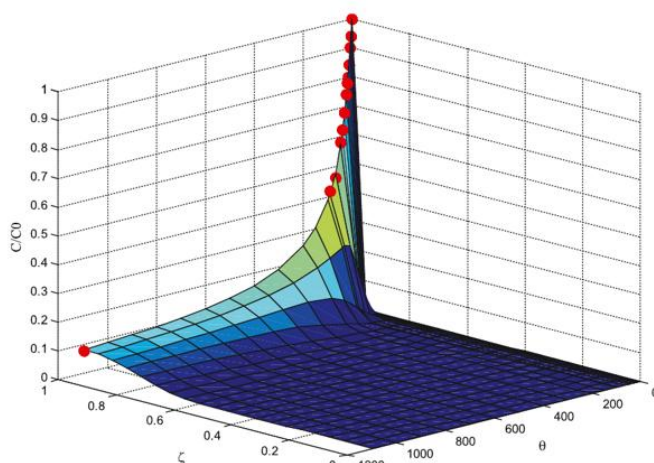


Figure 1- IPDM-predicted methylparaben concentration profile as a function of dimensionless time and radial coordinate. Red symbols represent experimental bulk concentration data.

Pore diffusivity decreased with alkyl ester chain length, and weighted regression yielded $D_p \propto V_{vdW}^{-0.53}$, closely matching the molecular-volume dependence reported for diffusion in dilute aqueous systems. This agreement provides an independent physical check on the fitted transport parameters.

Langmuir fitting showed that molar monolayer capacity was essentially independent of ester-chain length. A weighted fit gave $Q \approx 0.81 \text{ mmol g}^{-1}$ for all four parabens, suggesting that capacity is governed mainly by the common aromatic p-hydroxybenzoate core rather than by the alkyl substituent.

Equilibrium quantities inferred from kinetic fitting were compared with values obtained independently from adsorption isotherms. Agreement was particularly good for methylparaben, while ethyl- and propylparaben showed compensation between fitted equilibrium constant and uptake. Despite wider uncertainty for some parameters, the cross-check supported the consistency of the coupled IPDM-Langmuir framework.

Conclusions

The IPDM successfully described paraben adsorption kinetics and provided physically meaningful pore diffusivities. The model captured the effect of molecular size on transport and yielded equilibrium parameters broadly consistent with independent isotherm analysis. The nearly constant molar monolayer capacity also suggests a common contribution from the aromatic core. This framework provides a transferable basis for adsorption systems governed by pore diffusion.

P32. Agricultural Waste-Derived Carbon Materials for Pb (II) Removal from Water: Performance of Corncob Biochar and Magnetic Carbon Quantum Dot Hybrid

Amy Pamela Montiel Carrillo^{1*}, Araceli Jacobo Azuara², Guillermo Manuel González Guerra².

¹University of Guanajuato, Division of Natural and Exact Sciences, Noria Alta S/N, C.P. 36050, Guanajuato, Guanajuato, Mexico.

* ap.montielcarrillo@ugto.mx

Lead contamination in water remains a major environmental concern because of its toxicity, persistence, and bioaccumulation. This work investigates sustainable carbon-based adsorbents derived from corncob waste, including raw biomass, biochar, and a magnetic hybrid material containing carbon quantum dots and citric-acid-coated magnetite, for Pb (II) removal from aqueous solution. The materials were characterized to evaluate their surface chemistry, carbon structure, charge related properties, and functional groups involved in metal uptake. Batch adsorption experiments were performed at pH 4 using initial Pb (II) concentrations between 10 and 100 mg L⁻¹. Among the evaluated materials, biochar showed the highest removal efficiency, exceeding 92% throughout the studied concentration range and reaching an adsorption capacity of approximately 9.2 mg g⁻¹. The magnetic hybrid displayed lower adsorption performance but retained practical relevance because of its easy magnetic separation. These results highlight the importance of surface oxygen containing groups and biomass transformation in the development of recoverable adsorbents for water treatment.

Introduction

Water contamination by Pb (II) remains a major environmental challenge due to its high toxicity, persistence, and bioaccumulation in living organisms. Among the available treatment technologies, adsorption has attracted considerable attention because of its high efficiency, operational simplicity, and the possibility of employing sustainable, low-cost adsorbents [1]. Lignocellulosic biomass represents an attractive precursor for producing carbon-based materials with surface functionalities capable of binding heavy metal ions [2]. In this study, raw corncob, corncob-derived biochar, and a magnetic hybrid material based on carbon quantum dots (CQDs) and magnetite were developed and comparatively evaluated for Pb (II) adsorption from aqueous solutions.

Experimental

Corncob biomass was processed to obtain biochar through thermal treatment and carbon quantum dots (CQDs) via ultrasound-assisted exfoliation. A magnetic hybrid adsorbent was subsequently synthesized by coupling the CQDs with citric-acid-coated

magnetite nanoparticles. The obtained materials were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, point of zero charge (PZC), and zeta potential analysis to investigate their physicochemical properties. Batch adsorption experiments were conducted using Pb (II) solutions (10–100 mg L⁻¹) at pH 4 and room temperature with an adsorbent dosage of

0.1 g. Residual Pb (II) concentrations were determined by atomic absorption spectroscopy (AAS), and adsorption performance was assessed in terms of removal efficiency and adsorption capacity.

Results

As summarized in Table 1, biochar exhibited the highest Pb (II) adsorption performance, reaching a removal efficiency of 92.32% and a maximum adsorption capacity of 9.23 mg g⁻¹, followed by raw corncob (8.24 mg g⁻¹) and the magnetic hybrid (6.85 mg g⁻¹). The enhanced performance of biochar is attributed to the thermal treatment, which promotes the development of surface functionalities favorable for Pb (II) adsorption. Although the hybrid showed a lower adsorption capacity, its magnetic properties enable rapid separation and recovery from aqueous media. The adsorption isotherms (Figure 1) indicate that both the Langmuir and Freundlich models adequately describe the experimental behavior.

Table 1- Pb(II) adsorption performance at an initial concentration of 100 mg L⁻¹.

Material	Removal (%)	q _e (mg g ⁻¹)
Raw corncob	82.39	8.24
Biochar	92.32	9.23
Magnetic hybrid	68.52	6.85

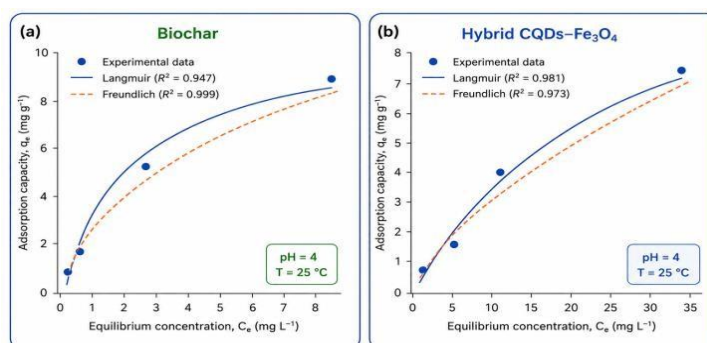


Figure 1- Experimental adsorption isotherms of Pb (II). Experimental adsorption data and Langmuir and Freundlich model fitting for (a) biochar and (b) hybrid CQDs–Fe₃O₄ at pH 4 and 25 °C.

Conclusions

Biochar derived from corncob showed the best Pb (II) adsorption performance among the evaluated materials. The magnetic hybrid exhibited a lower adsorption capacity but provided the additional advantage of magnetic recovery. These findings demonstrate the potential of corncob-derived carbon materials as sustainable adsorbents for water treatment and provide a basis for further optimization of magnetic hybrid systems.

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P33. ADSORPTIVE REMOVAL OF TETRACYCLINE HYDROCHLORIDE FROM AQUEOUS MEDIA USING BENTONITE AND HALLOYSITE CLAYS: EQUILIBRIUM, KINETIC, AND REUSE STUDIES

Aisha Pereira¹, João Gomes¹, Adriano Freitas¹, Leila Campos³, Enríque Rodríguez-Castellón², Daniel Plata-Ballesteros², Luciene Carvalho^{1*}

¹ Technology Energetic Laboratory (LABTEN), Federal University Rio Grande do Norte, Brazil

² Department of Inorganic Chemistry, Crystallography and Mineralogy, Faculty of Sciences, University of Málaga, Interuniversity Research Institute on Biorefineries (I3B), 29071 Málaga, Spain.

³ Postgraduate Program in Chemistry - PPGQ, Federal University of Bahia, Salvador 40170-110, Brazil

* Luciene.santos@ufrn.br

Abstract

Water contamination by tetracycline has encouraged the development of efficient and low-cost adsorbent materials. In this study, natural and modified bentonite and halloysite were evaluated for tetracycline removal from aqueous media using different characterization techniques. The adsorbents showed high adsorption efficiency, with removal rates above 98%, highlighting the potential of these clay minerals as promising materials for water treatment applications.

Introduction

Pharmaceutical residues, such as tetracycline, are considered emerging contaminants due to their persistence in aquatic environments and the low efficiency of conventional treatment methods. In this context, natural and modified clay minerals, such as bentonite and halloysite, have shown promising potential as low-cost and efficient adsorbents for contaminant removal from aqueous media [1,2,3,4].

Experimental

The study investigated the acid modification of natural clay minerals using HCl (1 mol.L⁻¹) at 60 °C for 4 h, followed by filtration, washing, neutralization, and drying. The adsorbents were characterized by XRD, XRF, TG, SEM, EDS, and XPS analyses to evaluate their structural, physicochemical, and compositional properties before and after modification. Adsorption performance was assessed through equilibrium and kinetic studies using Langmuir, Freundlich, Temkin, Sips, pseudo-first-order, pseudo-second-order, and Elovich models. Tetracycline adsorption experiments were performed using 25 mL of solution (25–500 mg.L⁻¹) and 0.3 g of adsorbents, with contact times from 1 min to 24 h. Final concentrations were determined by UV-Vis spectrophotometry at 360

nm. After adsorption, the materials were regenerated with 0.1 mol.L⁻¹ HCl and reused for seven adsorption cycles to evaluate reuse efficiency.

Results and discussions

Pharmaceutical residues, especially tetracycline, are considered emerging contaminants due to their persistence in aquatic environments and the low efficiency of conventional treatment systems. In this study, natural and acid-modified bentonite and halloysite were evaluated as adsorbents for tetracycline removal from aqueous media. Adsorption equilibrium and kinetic studies demonstrated that acid treatment significantly improved the adsorption performance of both clay minerals, increasing surface reactivity and adsorption capacity. Figure 1 shows the adsorption isotherms of both clay minerals. For bentonite, the modified material (BA1) reached removal efficiencies above 99% in only 30 min, with adsorption capacity close to 41 mg·g⁻¹. Equilibrium data showed better fitting to the Freundlich model ($R^2 > 0.9873$), suggesting adsorption in heterogeneous systems and multilayer formation, while the pseudo-second-order kinetic model ($R^2 \approx 0.999$) indicated chemisorption as the predominant adsorption mechanism. For halloysite, acid-treated samples showed superior adsorption performance compared to the natural material, increasing tetracycline removal from 92% to 98% while reducing adsorption time from 24 h to 6 h. The adsorption process presented better fitting to the Langmuir model ($R^2 > 0.9909$), indicating monolayer adsorption on homogeneous active sites, with an increase in maximum adsorption capacity from 2.12 to 3.05 mg·g⁻¹ after acid activation. Similar to bentonite, the pseudo-second-order model showed the best kinetic adjustment ($R^2 \approx 0.999$), reinforcing the predominance of chemisorption interactions between tetracycline molecules and the adsorbent surface. Reuse studies showed high stability of the adsorbents, with BA1 presenting only a 10–14% reduction after seven cycles, while acid-treated halloysite maintained removal efficiencies above 80% after four cycles. Maximum tetracycline removals reached 99% for BA1 and 98% for acid-treated halloysite, confirming the strong potential of these materials for wastewater treatment applications.

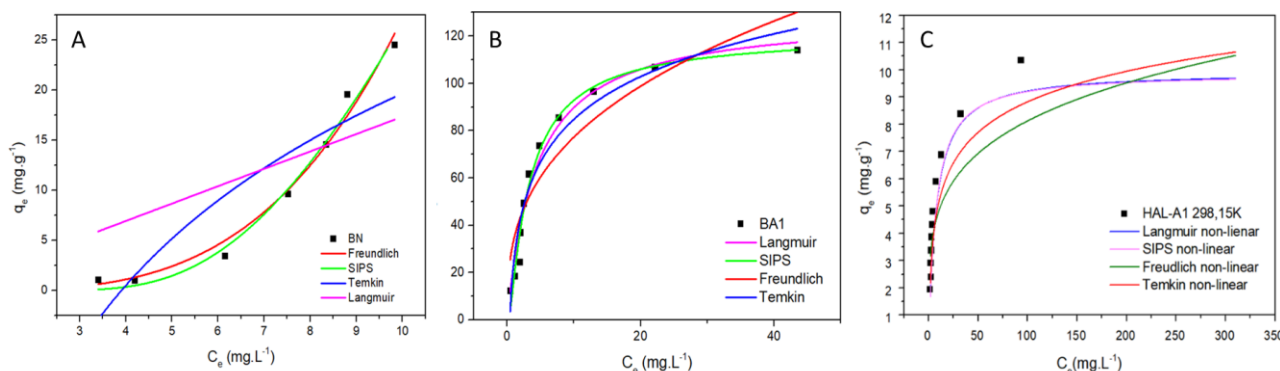


Figure 1 - Adsorption isotherms of bentonite at low concentration (A), bentonite at high concentration (B), and halloysite (C) for tetracycline removal from aqueous media.

Conclusion

The results demonstrated that both bentonite and halloysite are efficient adsorbents for tetracycline removal from aqueous media. Acid-modified bentonite (BA1) achieved removal efficiencies above 99% with adsorption capacity close to $41 \text{ mg}\cdot\text{g}^{-1}$, while acid-treated halloysite reached 98% removal efficiency and increased adsorption capacity from 2.12 to $3.05 \text{ mg}\cdot\text{g}^{-1}$. The adsorption process for both materials was better described by the pseudo-second-order kinetic model, indicating predominance of chemisorption mechanisms. Reuse studies showed good stability of the adsorbents, with BA1 presenting only a 10–14% reduction after seven cycles and acid-treated halloysite maintaining high adsorption efficiency after four cycles, confirming the potential of these materials as low-cost and sustainable adsorbents for wastewater treatment.

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