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Editorial

Adsorption Processes for CO_2 Capture from Biogas Streams

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Anaerobic digestion plays a starring role in the development of a bioeconomy due to the practical advantages that gaseous fuels have over solid fuels (i.e., handling, transportation, storage, and supply), together with the need to replace gaseous fossil fuels in multiple applications. Anaerobic digestion handles biodegradable waste biomass of different origins, such as animal wastes, sewage sludge, and organic municipal wastes, and, therefore, has great potential. The biogas generated by anaerobic digestion is mainly composed of CH_4 (53–70 vol.%) and CO_2 (30–47 vol.%), with smaller amounts of other gases, such as N_2, O_2, H_2, H_2O, CO, and H_2S [1]. Biogas is receiving considerable attention due to the possibility of injection into the natural gas grid, and its use as an alternative fuel for vehicles or as a renewable chemical feedstock. However, the CO_2 percentage in the biogas must be reduced to increase its calorific value and to avoid corrosion phenomena in the pipelines [2]. Different biogas upgrading technologies aim to separate methane from carbon dioxide and other components: water scrubbing [3], amine scrubbing [4], membrane separation [5], pressure swing adsorption [6], and recent trends biological systems [7], among others.

Adsorption processes, such as pressure swing adsorption (PSA), are ideal for biogas upgrading to obtain high-purity biomethane because they usually present lower energy requirements than other technologies [8,9]. The most important characteristics of a suitable adsorbent for CO_2/CH_4 separation include, wide availability, high CO_2 selectivity and adsorption capacity, stability, ease of regeneration, and low cost. The most popular adsorbents for biogas upgrading are activated carbons (ACs), activated alumina, metal oxides, zeolites, metal organic frameworks (MOFs), polymers and amine-based solid adsorbents [10].

This Editorial gathers recent research published in *Energies* to highlight the potential of adsorbents for biogas upgrading under realistic conditions. These studies focus on the development of alternative adsorbents to the commercially available with improved performance. Alvarez-Gutierrez et al. [11] studied the performance of phenol-formaldehyde (PF) resin-based activated carbons to separate CO_2 from several mixtures (CO_2/CH_4; CO_2/N_2, CO_2/H_2). Five microporous ACs were prepared from the PF resins, following carbonization in N_2 and ulterior activation in CO_2. The ACs were texturally characterized to determine their microporosity, which is of the utmost importance for CO_2 adsorption. A preliminary test was conducted to reject samples with less than 2 mmol/g of CO_2 adsorbed. To this end, CO_2 adsorption isotherms at 25 °C and up to 101 kPa were determined. Following this test, the ACs that were synthesized from Resol resin through a basic catalysis procedure were discarded. They presented CO_2 adsorption capacities below the 2 mmol/g CO_2 threshold, primarily due to their lower textural development (lower micropore volumes) in comparison with the ACs prepared from Novolac resin by an acid catalysis procedure. The single adsorption isotherms showed greater values of CO_2 adsorption compared to CH_4. Multicomponent adsorption from binary CO_2/CH_4 mixtures was predicted from the fitting of the single component adsorption data to the Sips model. The selectivity of the carbons to separate CO_2 from CO_2/CH_4 mixtures at ambient temperature and sub-atmospheric pressures was estimated from the predictions of the extended Sips model [12]. It was observed that the ACs prepared from Novolac resin and impregnated with a saturated KCl solution at ambient temperature (NKa-A82), showed the highest selectivity to CO_2/CH_4 among the

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tested carbons. This selectivity value (5.3) was even higher than that of a commercial AC, BPL, which was taken as a reference (3.9).

Abdeljaoued et al. [13] studied the separation of CO_2 from biogas effluents by using a coconut shell-based activated carbon (CNS). The production of the CNS AC entailed activation with CO_2 at 900 °C. Textural characterization of the adsorbent by N_2 physical adsorption at −196 °C and CO_2 at 0 °C was accomplished. In this way, the total pore volume (Vp), the apparent BET surface area, the micropore volume (W_0) and the average micropore width were determined. Physical activation in CO_2 produced an AC strictly microporous where the micropores (W_0) represented more than 85% of the whole volume of the pores (Vp), with a BET surface area of 1378 m^2/g and an average narrow micropore size, L_0, of 0.85 nm, as estimated from CO_2 adsorption. The performance of the CNS adsorbent for biogas upgrading was assessed with high-pressure CO_2 and CH_4 adsorption isotherms in a high-pressure magnetic suspension balance, at three temperatures (30, 50 and 70 °C) and pressures up to 10 bars. The performance of the activated carbon for CO_2/CH_4 separation under dynamic conditions was evaluated with breakthrough tests in a lab-scale fixed-bed column. After six consecutive adsorption–desorption cycles, the CNS-based activated carbon maintained its activity, showing perfect cyclability and regeneration under the evaluated conditions. The adsorption capacities of CO_2 and CH_4 of the produced activated carbon were 1.86 and 0.52 mol/kg, respectively, at 30 °C and 1 bar, with a selectivity for CO_2 over CH_4 of 3.6, comparable to other carbon-based adsorbents in the literature.

Textural properties and surface chemistry are two parameters driving the adsorption of CH_4 and CO_2 on activated carbons. In addition, the activation method influences the properties of the ACs and, consequently, their capacity to selectively adsorb methane and carbon dioxide. In this context, Peredo-Mancilla et al. [14] analyzed the influence of both the textural properties and surface chemistry of olive stone ACs on the adsorption of CH_4 and CO_2. Three ACs were produced by CO_2 physical activation (AC-CO_2), H_2O physical activation (AC-H_2O), and H_3PO_4 chemical activation (AC-H_3PO_4). Different textural properties were determined depending on the activation method; the AC-H_2O presented the highest total pore volume as a consequence of its higher volume of mesopores (0.30 cm^3/g), in comparison with 0.04 and 0.02 cm^3/g for AC-H_3PO_4 and AC-CO_2, respectively. A higher BET specific surface area (1178 m^2/g) and micropore volume (0.45 cm^3/g) were determined for AC-H_3PO_4 in comparison with the physically activated ACs (about 760 m^2/g and 0.30 cm^3/g). As the ACs' surface chemistry is of great importance for the adsorption process, the type and quantity of surface oxygenated groups were determined by temperature-programmed desorption coupled with mass spectrometry (TPD-MS). AC-H_3PO_4 presented higher amounts of oxygenated groups, mainly carboxylic acids, quinones and anhydrides. AC-H_2O showed surface oxygen groups in the form of phenol and carboxylic acids, while the formation of quinones, lactones and carboxylic acids took place on the AC-CO_2 surface. Measurement of CH_4 and CO_2 adsorption isotherms was undertaken for the three olive stone-based ACs up to a pressure of 3.2 MPa at 30 and 50 °C. The higher textural properties displayed by the AC obtained by chemical activation, AC-H_3PO_4, rendered higher CO_2 and CH_4 adsorption capacities than the physically activated ACs. Textural properties, rather than surface chemistry, were the determinant factors that most influenced the CO_2 capacity of adsorption. A comparison of the physically activated ACs showed that AC-H_2O gave higher CH_4 and CO_2 adsorption than AC-CO_2, despite both ACs presenting similar BET surface areas and micropore volumes. The higher CH_4 capacity of AC-H_2O was explained by its greater mesoporosity, while the higher amount of oxygen surface functionalities in AC-H_2O compared to AC-CO_2 supported its higher CO_2 adsorption.

MOFs with step-shaped isotherms are considered potential adsorbents for CO_2 capture and biogas upgrading. Ribeiro et al. [15] employed a Zn(dcpa) MOF (dcpa (2,6-dichlorophenylacetate)), that was reported to exhibit a dynamic behavior and stepwise adsorption, for the separation of CO_2/CH_4 mixtures. The Zn(dcpa) sample was characterized by power XRD, TGA, N_2 physisorption, and helium picnometry. In addition,

single-component adsorption isotherms of CO_2, CH_4, and N_2 at 0, 30 and 50 °C, between 0 and 35 bar, were determined. The TGA analysis indicated that the Zn(dcpa) was stable up to 373 °C. The potential of Zn(dcpa) for the separation of CO_2 from other gases, in particular CH_4, was evaluated by comparing the individual adsorption equilibrium isotherms and determining the separation selectivities. At 30 °C the CO_2/CH_4 selectivities decreased with the increasing pressure, ranging from 2.9 (at 1 bar) to 2.1 (at 6 bar). The authors compared the selectivities of Zn(dcpa) for CO_2/CH_4 with commercial MOFs MIL-53(Al), ZIF-8 and Fe-BTC. It was found that at low pressures Zn(dcpa) showed a higher selectivity than the other MOFs.

Zielinski et al. [16] came up with a new approach for biogas upgrading. In their laboratory-scale study they used biowaste material from wastewater treatment plants (i.e., the lime-stabilized excess sludge) as a natural sorbent for CO_2 separation from CH_4 in biogas streams. The research focused on the efficacy of CO_2 separation as a function of the inflow velocity of the raw biogas through a fixed-bed column reactor. The reactor was packed with anaerobic sludge treated with CaO, which was used as an active and inexpensive sorption material. The effect of the inflow biogas velocity on the CO_2 sorption capacity was studied in breakthrough experiments. At velocities between 5–20 mL/min, it was observed that the highest sorption capacities were achieved with biogas rates of 10 mL/min (110.03 mg/g or 2.51 mmol/g) and 15 mL/min (127.22 mg/g or 2.89 mmol/g). In all cases, the biogas stream was almost devoid of CO_2: the carbon capture took values over 98 vol%. The maximum biomethane concentration in the biogas outlet achieved a value of 98.9 vol% at a biogas inflow velocity of 15 mL/min, while the CO_2 concentration was practically zero (a value of 0.44 vol%).

The above-described studies highlight the potential of adsorbents for CO_2/CH_4 separation. Nevertheless, the optimum adsorbent selection will also entail factors such as the cost of production and the feasibility of scaling up. Future research should focus on validating the performance of the adsorbent under more realistic biogas conditions analyzing, for instance, the effect of the presence of water and other components, such as H_2S.

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