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Towards bio-upgrading of biogas: biomass waste-based adsorbents

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Abstract

The choice of an appropriate adsorbent for CO_2 separation by pressure swing adsorption remains a field of intense research and it would be of great help to rely on a parameter that could be used to quickly evaluate the performance of those materials. In this work, two activated carbons prepared in our laboratory from biomass wastes (olive and cherry stones) are studied for the separation of CO_2 from mixtures of CO_2 and CH_4. CO_2 and CH_4 adsorption isotherms at room temperature and up to 10 bar were determined in a high pressure magnetic suspension balance. Breakthrough adsorption experiments with simulated biogas binary mixtures were conducted in a fixed-bed lab-pilot adsorption unit. The performance of the tested carbons was assessed in terms of a dimensionless sorbent selection parameter (*S*), which is based on the selectivity but incorporates the nature of the adsorption isotherm under PSA operating conditions. A commercial activated carbon Calgon BPL was also tested and used as reference material for the separation process.

Experimental results show that the performance of the different adsorbents, based on the calculated *S* parameter, may be very different depending on whether data is derived from pure component adsorption isotherms or from breakthrough adsorption experiments. Under dynamic flow conditions, activated carbons produced in this study show a great potential to be applied to a CO_2/CH_4 separation for biogas upgrading purposes. Further research is envisioned in order to define a PSA process that maximizes the purity and recovery of CH_4.

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1. Introduction

In a world that is increasingly accepting the imperative nature of sustainable development, the junction of energy and environment has become a field of intense activity. Biogas, naturally occurring from the decomposition of organic wastes, has yielded important industrial applications, and its commercial value has risen for two reasons: (i) its release into the atmosphere contributes largely to greenhouse gas concentration, with consequent and significant remediation costs, and (ii) its energetic content is high, and its exploitation means significant revenues or avoided costs.

Nomenclature

α_{ab}	selectivity
Δm	reading of the high pressure balance
ρ	density of the atmosphere surrounding the sample
m	surface excess mass adsorbed
P	pressure
q	uptake
T	temperature
STP	standard pressure and temperature (1 bar, 0 ºC)
V	volume of the adsorbent sample displacing the atmosphere
V_{SC}	volume of the balance components holding the sample
WC	working capacity

Biogas is rich in CH_4 (typically ranging between 35 and 75 vol.%), and its higher heating value is between 15 and 30 MJ Nm^{-3}. CO_2 in biogas is considered a nuisance because it is present in large quantities (almost balanced between about 95% and the percentage of CH_4), and it is an inert gas in terms of combustion, thus decreasing the energetic content of biogas [1]. To increase the energy content and also to avoid the pipeline and equipment corrosion, the CO_2 content for pipeline grade biomethane should be less than 2-3%. The technology most widely used for carbon dioxide removal is amine absorption, but amine plants are complex and costly. Membrane systems also have been used for this purpose and, within certain process conditions, can be an attractive alternative. However, one challenge for membrane systems is reaching the allowable carbon dioxide levels required by the pipeline system. For this reason, membrane systems are sometimes integrated with further processing. Another alternative is the removal of carbon dioxide by means of an adsorption process. Pressure swing adsorption (PSA) technology has gained interest due to low energy requirements and low capital investment costs [2]. Indeed, adsorption-based processes using microporous materials are a very promising cost-efficient technology, particularly in separation systems such as PSA, which is commonly accepted to be the most attractive, efficient and affordable due to its simple control, low operating and capital investment costs, and higher energy efficiency [3].

Activated carbons present relevant features to be promising candidates for CO_2/CH_4 such as their hydrophobic character, their relative lower cost and reduced energy requirements for regeneration. Its demand is growing as a result of environmental requirements and new areas of application. Biomass is commercially used as an activated carbon precursor; due to the unavailability of the main basic materials like hard coal, wood or coconut shells, in many countries other biomass matters are being tested for their appropriateness for activated carbon production. Olive stones and cherry stones are suitable raw materials for preparation of activated carbons with high adsorption capacities, sufficient mechanical strength, and low ash contents. Detailed information about carbon production from biomass sources can be found elsewhere [4].

2. Experimental

2.1. Materials

The biomass waste-based activated carbons were produced in our laboratory using olive stones (OS) and cherry stones (CS) as carbon precursors. The proximate and ultimate analyses of these carbon precursors are presented in Table 1. These materials present great similarities characterised by low ash contents, suitable for activated carbon production, and high oxygen contents attributed to the volatile matter.

Table 1. Proximate and ultimate analyses of OS and CS.

Carbon precursor	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, daf)				
	Volatile mater	Ash	Fixed carbon	C	H	N	S	O
OS	85.4	0.6	14.0	51.6	6.0	0.1	0.6	41.7
CS	82.8	0.4	16.8	52.7	6.2	0.6	0.0	40.5

db: dry basis; daf: dry ash free basis

Activated carbons were produced by means of CO_2 activation. For the olive stones derived carbon (OS-AC) a conventional two-step procedure was pursued, including prior carbonization under inert atmosphere followed by activation in CO_2. More details on the production of this sample can be found in a previous paper from our group [5]. It must be noted that this sample was produced by addition of a phenol-formaldehyde resin to the olive stones prior to carbonization and subsequent activation in CO_2.

In the case of the cherry stones based carbons (OS-AC) a single-step procedure was preferred. This means that the sample is not previously carbonized but directly activated in CO_2. Single-step activation of biomass with steam [6] or CO_2 [7] has shown to produce good quality biomass-based activated carbons, with similar or even better characteristics than those obtained by the more conventional two-step procedure. These two carbons together with the reference commercial BPL were characterized in terms of CO_2 adsorption isotherms at 0°C, that allow the assessment of the narrower microporosity (pore sizes < 1 nm). The use of CO_2 as a probe molecule at 0°C is recommended for the characterization of the narrow micropores to avoid underestimation of the pore volume by N_2 adsorption at -196 °C. Isotherms were determined in a Quantachrome Nova 4000 volumetric device. Prior to analysis the three samples were outgassed overnight at 120°C under vacuum. Table 2 summarizes the estimated parameters.

Table 2. Textural characterization by means of CO_2 adsorption at 0°C.

Carbons	W_0 (mL g^{-1})	S_{mi} (m^2 g^{-1})	L_0 (nm)
OS-AC	0.33	925	0.72
CS-AC	0.34	903	0.76
BPL	0.39	983	0.80

The micropore volume (W_0) was determined by the Dubinin-Radushkevich (DR) equation [8]. The average micropore width (L_0) was calculated through the Stoeckli-Ballerini equation [9]. The micropore surface area (S_{mi}) stems from a relation between W_0 and L_0, assuming slit shaped micropores. All three samples show similar features, particularly the biomass based carbons.

2.2. High pressure CO_2 and CH_4 adsorption isotherms

CO_2 and CH_4 adsorption isotherms at room temperature and up to 10 bar were determined in a high pressure magnetic suspension balance, Rubotherm-VTI. This instrument allows the elimination of most of the disadvantages of the gravimetric technique by physically separating the sample and the high resolution balance by means of a magnetic suspension coupling. The sample is exposed to the measuring atmosphere while the balance is located

under ambient conditions [10]. High resolution (0.01 mg) sorption measurements can be performed in the pressure range from ultra high vacuum to 500 bar at temperatures between -3 and 227 ºC.

Common measuring techniques for adsorption equilibrium allow only differences to be measured, i.e., the mass of adsorbate minus the product of the volume of the atmosphere displaced by the adsorbent and the density of the atmosphere surrounding it. Thus, to obtain the quantity of interest, the mass of adsorbate (m), from the measured data, a buoyancy correction has to be performed:

$$m(P, T) = \Delta m(P, T) + (V_{SC} + V)\, \rho(P, T) \tag{1}$$

In order to obtain a value for the volume of the adsorbent, the so-called helium volume was determined. Therefore, we have performed measurements with He as adsorptive gas. Applying eq. (1), and assuming He is not adsorbed, the volume of the adsorbent can be calculated from the measured data [11].

2.3. Fixed-bed binary CO_2/CH_4 adsorption experiments

Dynamic breakthrough experiments were conducted in a purpose built fixed – bed adsorption unit. The scheme and detailed description of the system can be found in a previous work [12].

A simulated biogas binary CO_2/CH_4 mixture (50/50 vol. %) was fed (30 mL min^{-1} STP) to the adsorption unit and the adsorption performance of the samples was evaluated at room temperature in the 3 to 10 bar pressure range. For each sample and pressure six consecutive adsorption-desorption cycles were conducted where adsorption proceeded until saturation and desorption was extended to full regeneration of the carbons. Effluent gas analysis was performed by means of a dual channel micro-gas chromatograph fitted with a thermal conductivity detector. During the adsorption stage the CO_2 and CH_4 concentrations in the column effluent gas were continuously monitored as a function of time -breakthrough curve- until the composition approached the inlet gas composition value, i.e., until saturation was reached. The specific equilibrium amounts of adsorbed CO_2 and CH_4 under a specific temperature and CO_2 and CH_4 partial pressures can be determined by applying a mass balance equation to the bed but taking into consideration the gas accumulated in the intraparticle voids and dead space of the bed. More details about the calculation procedure can be found in [12].

2.4. Calculation of parameter S

A simple parameter is proposed for comparing the performance of the three adsorbents for this particular binary CO_2/CH_4 gas separation by means of pressure swing adsorption. This dimensionless sorbent selection parameter, S, was first proposed by Rege at al. [13]. It is based on the ratio of the working capacities (delta loadings, i.e., differences in adsorbed amount at high and low pressures) of the two gases, WC_a/WC_b, and the equilibrium selectivity (α_{ab}) of the sorbent for CO_2:

$$S = \frac{WC_a}{WC_b}\, \alpha_{ab} \tag{2}$$

The equilibrium selectivity should also be normalized to the composition of the gas mixture as shown in eq. (3), where q_a is the uptake and P_a is the partial pressure of component a [14]:

$$\alpha_{ab} = \frac{q_a/q_b}{P_a/P_b} \tag{3}$$

For a given separation, the adsorbent that yields the highest S value may be the selected sorbent. This parameter has the attributes to be used for the selection of an adsorbent: it is readily estimated without complicated calculations

and it incorporates the essential nature of the isotherms under the PSA operating conditions. It has been previously reported that the working capacity is equally as important as selectivity in optimizing an adsorbent for pressure-swing adsorption [15].

3. Results and discussion

Table 3 summarizes the CO_2 and CH_4 uptakes of the tested samples determined from the high pressure pure adsorption isotherms, for a binary mixture of 50/50 vol.% CO_2/CH_4. An estimation of the parameter S for each selected total pressure is also included assuming that desorption occurs at the lowest total pressure of 3 bar.

Table 3. S parameter calculated from high pressure pure CO_2 and CH_4 adsorption isotherms.

P total (bar)	OS-AC			CS-AC			BPL		
	CO_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	S	CO_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	S	CO_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	S
3	2.79	1.31	-	2.89	1.45	-	2.27	0.99	
6	3.75	1.89	3.28	4.04	2.09	3.29	3.38	1.58	4.02
10	4.51	2.36	3.13	4.97	2.66	3.15	4.43	2.15	3.84
18	5.34	2.94	2.84	6.04	3.39	2.89	5.84	2.94	3.64

As expected, CO_2 and CH_4 uptakes increase with pressure and all tested adsorbents exhibit strong adsorption preference to CO_2 over CH_4. Amongst all the sorbents, cherry stones-based activated carbon presents the greatest CO_2 and CH_4 uptakes; however, calculated values of parameter S indicate that the commercial activated carbon, BPL, would better perform the separation of CO_2 and CH_4, according to the data from the pure component CO_2 and CH_4 adsorption isotherms. A common feature for all the sorbents is the fact that S decreases with increasing pressures, i.e., the separation of a 50/50 vol.% CO_2/CH_4 mixture at room temperature would be enhanced at lower values of total pressure.

The equilibrium adsorption capacities of BPL and OS-AC were further tested under dynamic flow conditions in a fixed-bed adsorption unit. The characteristics of the bed are presented in Table 4 below.

Table 4. Bed characteristics for the breakthrough experiments.

	OS-AC	BPL
Mass of adsorbent (g)	2.78	2.40
Particle size (mm)	1-3	2-4.75
Total porosity (ε_T)	0.78	0.80
Bed diameter (cm)	0.9	0.9
Bed height (cm)	9.9	9.15
Bed density (g cm^{-3})	0.442	0.412

Breakthrough curves at room temperature and two different pressures, 3 and 10 bar, were then obtained for a 50/50 vol.% CO_2/CH_4 binary mixture. The adsorption pressure affects the shape of the breakthrough curve (Figure 1) as well as the breakthrough time (time required for the CO_2 concentration front to reach the bed outlet). For a given temperature and feed concentration, longer breakthrough times are observed at higher adsorption pressures for both, CO_2 and CH_4 profiles. At any pressure, the less adsorbed component of the gas mixture, CH_4, always breaks first than CO_2; additionally, a so-called roll-up effect is exhibited in their corresponding breakthrough curves (Figure 1b), where the concentration of CH_4 at the column exit temporarily exceeds the feed concentration. This is due to the displacement of initially adsorbed CH_4 by incoming CO_2.
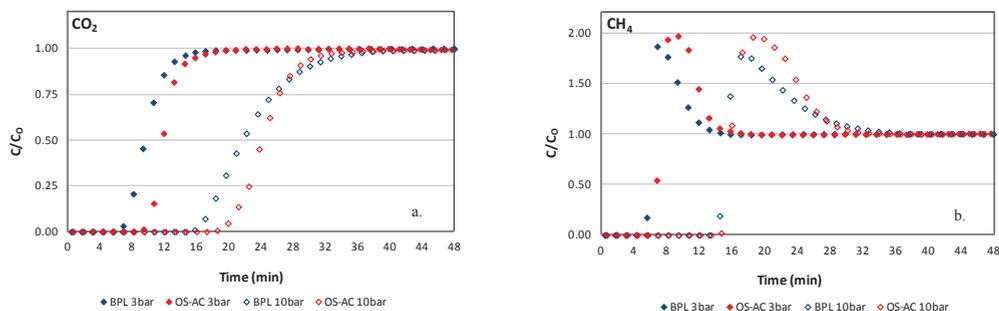
Figure 1. Breakthrough curves of a 50:50 vol.% CO_2/CH_4 gas mixture over BPL and OS-AC adsorbents at room temperature, 3 and 10 bar: (a) CO_2, (b) CH_4.

The obtained breakthrough curves are translated into dynamic uptake capacity by integration, with longer breakthrough times yielding higher uptake capacities (Table 5). The parameter S was also estimated from CO_2 and CH_4 uptakes and selectivity values derived from the dynamic tests (Table 5) and, in this case, the biomass waste-based activated carbon showed a larger value of *S* than the commercial BPL carbon.

Table 5. *S* parameter calculated from the breakthrough adsorption experiments.

| Adsorbents | 3 bar | | | 10 bar | | | Parameter *S* |
| | Uptake (mol kg^{-1}) | | $\alpha_{CO2/CH4}$ | Uptake (mol kg^{-1}) | | $\alpha_{CO2/CH4}$ | |
	CO_2	CH_4		CO_2	CH_4		
OS-AC	2.53	0.64	3.73	5.12	1.51	3.13	9.36
BPL	2.46	0.70	3.31	4.87	1.65	2.71	6.83

In a dynamic operation, OS-AC would then perform much better to efficiently separate a CO_2/CH_4 gas mixture by pressure swing adsorption for biogas upgrading purposes. It is therefore imperative to investigate, at a very initial stage, the dynamic behavior of any adsorbent intended to be used in a PSA process, as screening studies only based on pure adsorption isotherms could lead to a mistaken initial approach.

4. Conclusions

Separation of carbon dioxide and methane via biomass waste-based activated carbons is investigated using a dimensionless sorbent selection parameter, *S*, which allows us to perform an initial screening of appropriate adsorbent materials for biogas upgrading applications. Two different adsorbents obtained from olive and cherry stones, OS-AC and CS-AC respectively, were assessed both, in a high pressure magnetic suspension balance and in a lab-scale fixed-bed reactor. A commercial activated carbon, Calgon BPL, was also studied as a reference material and for comparison purposes.

Upon calculation of the herein defined parameter, *S*, results showed a completely different adsorbents' behavior: according to data from the pure component CO_2 and CH_4 adsorption isotherms, the commercial BPL carbon would perform better for the intended PSA process than any of our synthesized biomass waste-based adsorbents. However, when the olive stones-derived activated carbon is compared with BPL under dynamic flow conditions, it is the former the one presenting a higher value of *S*, i.e., the most promising one when it comes to efficiently separate the CO_2/CH_4 gas mixture at given conditions. It is undoubtedly essential to take into account the dynamic performance of the adsorbents.

Under dynamic flow conditions, activated carbons produced in this study proofed to show a great potential to be applied to a CO_2/CH_4 separation for biogas upgrading purposes. Further research is envisioned in order to define a PSA process that maximizes the purity and recovery of CH_4.

Acknowledgements

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