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Simplistic approach for preliminary screening of potential carbon adsorbents for CO_2 separation from biogas

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ABSTRACT

The design of a pressure swing adsorption (PSA) system requires the development of a complex model that can describe the dynamics of adsorption in a fixed-bed, which means a labor intensive and time consuming work, especially when several adsorbents are going to be compared. Therefore, it would be very useful to establish a simple procedure to quickly assess the performance during the early stages of PSA systems design. The aim of this work is to develop a simplistic approach that drives the decision-making process on the adsorbent in a shorter time. A combined experimental and numerical study of CO_2/CH_4 adsorption is presented. Thus, three commercial activated carbons are compared in their performance to separate CO_2 from biogas under PSA conditions by means of equilibrium adsorption data. A straightaway model, developed to approach PSA systems in a very simple way, where the only input is equilibrium of adsorption data, has been adopted. The Adsorption Figure of Merit (AFM), CO_2 purity and CO_2 recovery were selected as performance indicators and they have pointed out one of the activated carbons, MC27, as the most promising adsorbent candidate to separate CO_2/CH_4 by means of PSA. A sensitivity analysis of the process performance as a function of the bed dimensions has been addressed using the developed short-cut model.

1. Introduction

Pressure Swing Adsorption (PSA) is widely deployed at commercial scale for separation and purification of gases due to its low energy requirements, low capital investment cost, and safety and simplicity of operation [1]. In PSA operation gas separation is achieved by exploiting the affinities of gaseous components to adsorb on solid sorbents at different pressures. Gas separation could occur due to the aforementioned differences in adsorption affinity of gas species (equilibrium separation) or to differences in diffusion rates (kinetic separation) [2]. PSA operates in cyclic mode through high pressure adsorption and low pressure desorption steps in beds packed with adsorbent. Compression and vacuum generation therefore constitute the main energy requirements of the process [3]. Basically, the performance of a cyclic adsorption-desorption system is controlled by the overall dynamics of the fixed-bed and it has to be designed to increase the working capacity of the adsorbent, the net product purity and recovery of the desired product gas and to decrease the energy required for the regeneration [4].

The basic cycle configuration of a PSA system was described for the first time by Skarstrom in 1960 and it includes four steps (adsorption, blow-down, purge and pressurisation) implemented in two or more columns to allow continuous treatment of feed gas [5]. The set of stages or steps is termed as “cycle” and it usually serves as a benchmark to address the evaluation of a PSA operation [6]. In order to enhance process performance, most PSA systems incorporate extra steps in addition to the basic four-step PSA configuration. The introduction of a pressure equalization step developed at ESSO Research group [7] or the depressurization of the bed co-currently to the feed to remove part of the light component before blow-down [8] are some examples.

PSA technology has a broad range of applications: hydrogen purification [9–11], air separation [12,13], CO_2 removal [14,15], noble gases (He, Xe, Ar) purification [16,17], biogas upgrading [18–21], and so forth. In the last decades, biogas has received attention as renewable energy gas resource. Biogas is produced from the bacterial decomposition of organic wastes, and it contains mainly CH_4 and CO_2, while other contaminants (H_2S, NH_3, O_2, N_2, water vapour) rarely exceed the threshold of 4%. Since the amount of CO_2 in the biogas is quite significant (30–65%), its content must be reduced to increase the heating value of methane and to avoid pipeline and equipment corrosion in the presence of water [22].

Biogas upgrading is intended to obtain biomethane. To meet the same pipeline specifications than those of natural gas in terms of methane purity, the carbon dioxide content needs to be significantly reduced ($CO_2 < 3\%$ by volume). PSA is a feasible technology to do it with

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relatively low energy consumption [23]. After original work by Sircar in the late 1980s [18], many studies have developed PSA processes aimed at separating CO_2 from gaseous streams containing CH_4 [22,24,25]. A variety of microporous materials, such as activated carbons (ACs), zeolites and metal-organic frameworks (MOFs), have been considered for carrying out CO_2 separation [26–28]. Zeolites are the most extensively studied and commercially used CO_2 adsorbents, due to their stability at high temperatures and pressures and high selectivity to CO_2. However, activated carbons show high adsorption capacity at atmospheric pressure and present important advantages over zeolites, such as large surface area, high micropore volume, hydrophobic character, significant lower cost and reduced energy demand for regeneration [29].

Detailed design of a PSA system requires the development of complex models to describe the dynamics of adsorption in a fixed-bed, taking into account the mass, momentum and energy balances, and the kinetic and equilibrium equations. The heat and mass transfer coefficients, heat capacity, heat of adsorption, physical properties such as adsorption isotherms, porosity and void fraction of adsorbent, and many others are needed. However, the estimation of all these parameters from experiments is usually not straightforward and involves tedious and time consuming protocols. Thus, it is of utmost importance to figure out simplistic approaches that quickly assess PSA systems with high reliability in the early stages of process design [30], especially if a number of potential materials needs to be differentiated.

Therefore, the aim of the present work is to establish a simple procedure to quickly assess the adsorption performance during the initial stages of a PSA system design in order to develop a simplistic approach that allows fast decision-making on the adsorbent. This model may be too simplistic for detailed process design in industrial applications but relevant to bench-scale evaluation of adsorbents. The most common way to evaluate adsorbents in any potential application is to run isotherm tests to obtain equilibrium of adsorption data. This work develops a simple and straightforward model to assess the performance of three commercial activated carbons to separate CO_2/CH_4 in PSA operation, which only requires a fundamental study of the equilibrium of adsorption of CO_2 and CH_4. Thus, this methodology may help to speed up decision making on the selection of adsorbents during the first stages of a PSA system design, hence avoiding the complex and tedious dynamic simulation of the PSA process for all the potential adsorbent candidates.

2. Materials and methods

2.1. Materials

Two commercial activated carbons supplied by Calgon Carbon® (208C and BPL6 × 12) and an activated carbon developed by Mast Carbon International (MC27) were selected as adsorbent materials. These three ACs were tailored-produced for CO_2 adsorption. Indeed, 208C and BPL6 × 12 are particularly intended for CO_2/CH_4 separation. 208C is a granular activated carbon manufactured from coconut shells by high temperature steam activation, BPL6 × 12 is a bituminous coal-based carbon activated at a high temperature with steam, whereas MC27 is a phenolic resin-based extruded carbon prepared using polyethylene glycol as a binder and activated with carbon dioxide.

The activated carbons were characterised by physical adsorption of N_2 at -196 °C and CO_2 at 0 °C using volumetric devices from Micromeritics. The samples were outgassed overnight at 100 °C under vacuum prior to adsorption measurements. The apparent surface area was estimated from the N_2 adsorption isotherms at -196 °C by means of the Brunauer–Emmett–Teller (BET) equation in the relative pressure range 0.01-0.1 [31]. The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99, and the micropore volume (W_0) was determined by the Dubinin-Radushkevich (DR) equation [32]. The average micropore width (L_0) of the locally slit-shaped micropores was calculated by means of the Stoeckli-Ballerini relation [33]. Moreover, the micropore volume corresponds to $W_0 = (S_{mic}/2)L_0$, assuming a slit-shaped geometry and, consequently, the surface area of the micropore walls (S_{mic}) can be estimated by the geometrical relation [34]:

$$S_{mic}\ (m^2g^{-1}) = 2000W_0(cm^3g^{-1})/L_0(nm) \tag{1}$$

Table 1
Textural characteristics of the activated carbons.

	Activated carbon		
	208C	BPL6 × 12	MC27
N_2 adsorption at -196 °C			
BET surface area ($m^2\,g^{-1}$)	1406	1006	1330
Total pore volume ($cm^3\,g^{-1}$)	0.59	0.50	0.52
Micropore volume ($cm^3\,g^{-1}$)[a]	0.51	0.36	0.51
Average micropore width (nm)[b]	1.06	1.12	0.78
Micropore surface area ($m^2\,g^{-1}$)	950	634	1319
CO_2 adsorption at 0 °C			
Narrow micropore volume ($cm^3\,g^{-1}$)[a]	0.31	0.28	0.50
Average narrow micropore width (nm)[b]	0.87	0.86	0.76
Narrow micropore surface area ($m^2\,g^{-1}$)	720	661	1315

[a] Evaluated with the Dubinin-Radushkevich equation.
[b] Determined with the Stoeckli-Ballerini relation.

Table 1 summarises the main characteristics of the evaluated adsorbents. Activated carbons 208C, BPL6 × 12 and MC27 present high apparent BET surface areas (1406, 1006 and 1330 $m^2\,g^{-1}$, respectively) and well-developed microporosity (micropore volume of 0.51, 0.36 and 0.51 $cm^3\,g^{-1}$, respectively, assessed from the DR equation applied to the N_2 adsorption isotherms at -196 °C), as well as narrow micropore volumes of 0.31, 0.28, and 0.50 $cm^3\,g^{-1}$, respectively, determined from the DR relation applied to the CO_2 adsorption isotherms at 0 °C. This parameter has been pointed out as critical to the CO_2 adsorption capacity of solid sorbents at atmospheric pressure [35].

2.2. Pure gas component adsorption isotherms

The adsorption isotherms of pure CO_2 and CH_4 were measured up to 1000 kPa at 30 °C in a high pressure magnetic suspension balance (Rubotherm-VTI). The absolute amounts of CO_2 and CH_4 adsorbed over the pressure range tested were estimated following the procedure described in previous works [36,37]. Experiments with helium were carried out in order to determine the volume of the adsorbent and cell system, enabling the effect of buoyancy on the measurements to be evaluated. The experimental procedure and details on the set-up can be found in Martín et al. [38].

The extended Sips model was chosen to account for the equilibrium of adsorption of CO_2/CH_4 mixtures on the three activated carbons in the PSA model developed. To optimise the corresponding parameters of the extended Sips equation, the pure component CO_2 and CH_4 experimental adsorption isotherms were fitted to the Sips model [39] according to the following expression:

$$q = q_s\frac{(b_i\,P)^{1/n}}{1 + (b_i\,P)^{1/n}} \tag{2}$$

where q represents the concentration of the adsorbed species, P is the equilibrium pressure and q_s, b_i and n are the maximum adsorption capacity, the adsorption equilibrium constant and the parameter indicating the heterogeneity of the system, respectively. The value of n is usually greater than unity and the larger it is, the more heterogeneous the system is.

The fitting of the experimental data to the Sips model was conducted by means of the Solver Excel tool departing from values of q_s, and n of 1 and b_i of 0. In order to preserve thermodynamic consistency, CO_2 and CH_4 adsorption data were simultaneously fitted with common