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Post-combustion CO₂ capture adsorbents from spent coffee grounds

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Abstract

Post-combustion CO₂ capture can contribute to mitigate anthropogenic CO₂ emissions in the short-to-medium term at relatively low technology risk. However, there are not post-combustion units installed yet on a commercial scale, and the considered first generation capture processes, based on absorption with amines, are energy intensive. Adsorption processes present scope for reducing the energy penalty of the capture step. In this work, carbons prepared from spent coffee grounds are evaluated as potential adsorbents for this application. They present high CO₂/N₂ selectivity, and a working capacity competitive to that of zeolite 13X with the appealing advantages of a significant lower cost, higher stability and easier regeneration.

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Adsorption; CO₂ capture; post-combustion; activated carbon; coffee residues

1. Introduction

Carbon Capture and Storage (CCS) will play a vital role in worldwide efforts to limit global warming; in the least-cost efforts scenario, CCS will contribute to 19% of required emissions reduction by 2050 [1]. Post-combustion CO₂ capture is one of the different mitigation options for anthropogenic CO₂ emissions. This technology aims to separate the CO₂ present in flue gases produced at large stationary sources, to safely store it in geologic reservoirs avoiding its release to the atmosphere. The main advantages of this mitigation option are that existing power and industrial facilities could be retrofitted (given some requirements), and that the technology risk is lower than in alternative technologies [2]. The separation of CO₂ from flue gases can be carried out by different processes: absorption, adsorption, separation with membranes, cryogenic distillation, *etc.* [3]. Although there are not post-combustion units installed on a

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commercial scale yet, the considered first generation capture processes are based on absorption with amines, which are energy intensive due to the heat required to regenerate the solvent. Different adsorption processes, such as pressure swing adsorption (PSA), temperature swing adsorption (TSA) and combinations of them are being studied in an attempt to reduce the energy penalty of the capture step [4-8]. Research focus has also been made in the adsorbent side; silicas, zeolites, activated carbons, metal organic frameworks, *etc.*, are being evaluated worldwide for this application [9-11]. Among them, activated carbons present a series of advantages such as ease of regeneration, low cost, and high stability in flue gas conditions [7].

The use of abundant waste products from industrial and agricultural activities for the production of low-cost activated carbons is an appealing option. Biomass-based activated carbons have good properties, comparable to those obtained with other precursors, such as coal or petroleum coke, and present multiple applications in medicine, engineering, environment, *etc.* Moreover, using biomass as feedstock would reduce the carbon footprint of the adsorbent production process, due to the CO₂ fixed during the biomass growth. Different biomass feedstock has been evaluated for preparing CO₂ adsorbents: olive stones, almond shells, and coffee grounds, among others [12-17].

Coffee is considered the second largest traded commodity in the world. The International Coffee Organization estimates that 1.6×10^9 cups of coffee are drunk worldwide every day, and for each cup of coffee, around 10 g of coffee is brewed. Total production crop in 2010/2011 accounted for 134.2 million bags (trade of “green” coffee is made on a 60 kg bags basis) [18]. Instant coffee production consumes around 20% of the global production of green coffee beans and for each kg of soluble coffee produced near 0.9 kg of coffee grounds are obtained [19]. These residues are usually used as fuel in boilers or used for compost production [20]. However, recycling spent coffee grounds for the production of activated carbons is in the foreground in the hierarchy of waste management (Waste Framework Directive 2008/98/EC). If the preparation conditions are adequately controlled, it is possible to prepare activated carbons from spent coffee grounds with tailored properties in terms of micro texture and surface area [15]. In this study, the potential application of these carbons as adsorbents in post-combustion conditions is evaluated.

2. Materials and methods

Two microporous activated carbons obtained from spent coffee grounds by activation with CO₂ and KOH, NCHA29 and NCLK3, respectively, are the subject of the present study (preparation details and sample characterization can be found elsewhere [15]).

The equilibrium of adsorption of pure CO₂ and N₂ on the coffee based carbons was measured between 0 and 120 kPa at 0, 25 and 50°C in a volumetric apparatus, TriStar 3000 from Micromeritics. Prior to the adsorption measurements the samples were evacuated overnight at 100°C.

3. Results and discussion

3.1. Equilibrium of adsorption

The adsorption isotherms of pure CO₂ at 0, 25 and 50°C on samples NCLK3 and NCHA29 are shown in Fig. 1. Adsorption showed fully reversible by lowering the pressure (desorption path not shown) as

expected for physisorption processes. NCLK3 presents higher CO₂ uptake than NCHA29 over the entire temperature and pressure range due to its higher ultramicropore volume (0.36 vs. 0.25 cm³g⁻¹ [15]).

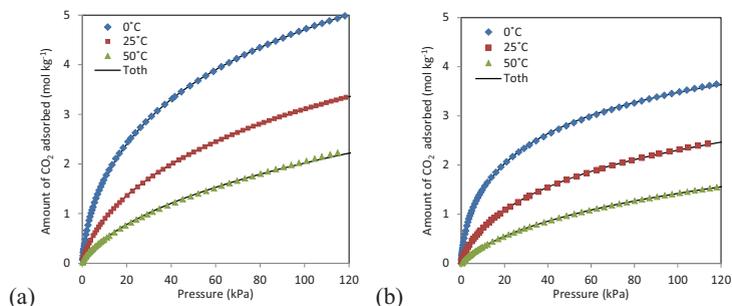


Fig. 1. CO₂ adsorption isotherms at 0, 25 and 50°C of samples NCLK3 (a) and NCHA29 (b).

The isosteric heat of adsorption of CO₂ was estimated from the experimental adsorption isotherms making use of the Clausius-Clapeyron equation:

$$Q_{st} = -R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_n \quad (1)$$

where Q_{st} is the isosteric heat of adsorption at an adsorbed amount n , T is the temperature, P is the pressure of the gas phase and R_g the universal constant of gases. Plotting $(\ln P)$ against $(1/T)$ at constant adsorbed amounts (isostere) yields a straight line which slope is equal to: $-Q_{st}/R_g$ (Fig. 2).

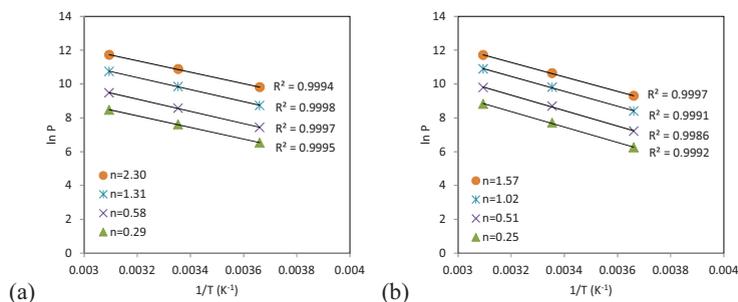


Fig. 2. Adsorption isosteres of CO₂ on NCLK3 (a) and NCHA29 (b).

On average, the isosteric heat of adsorption of CO₂ on NCLK3 and on NCHA29 is 27.19 and 36.42 kJ mol⁻¹, respectively. For carbon materials (essentially nonpolar adsorbents), the isosteric heat of adsorption depends mainly on the pore size distribution and secondly on the surface chemistry: values between 16 and 30 kJ mol⁻¹ have been reported for different types of commercial activated carbons [21, 22]. The higher value of sample NCHA29 compared to that of NCLK3 can be attributed to the narrower character of its microporosity [15]. Although the isosteric heat of adsorption of CO₂ on NCHA29 is relatively high, it is still below of that of zeolite 13X (40 kJ mol⁻¹ [23]), which arises from the stronger electrostatic interactions between the CO₂ molecule and the polar surface of the zeolite. The higher the

isosteric heat of adsorption, the greater thermal effects will be expected during pressure swing adsorption (PSA) operation (reduction of the working capacity).

Adsorption models are very useful as they can predict the behaviour of the equilibrium of adsorption in a wide temperature and pressure operation range (by interpolation or extrapolation of the data obtained by direct measurement). The Toth model [24] is commonly used due to the simple form of its equation (2) and its correct behaviour at low and high pressures:

$$n = n_m b P / [(1 + (bP)^t)^{1/t}] \quad (2)$$

n represents the concentration of the adsorbed phase, n_m the saturation capacity, P the pressure of the gas phase, t a parameter that represents the system heterogeneity ($t \leq 1$) and b is the affinity constant which is considered temperature dependent according to Equation 3 [25]:

$$b = b_0 \exp[Q/R_g T_0 ((T_0/T) - 1)] \quad (3)$$

where b_0 is the affinity at a reference temperature T_0 (taken here as 0°C), Q is a measure of the heat of adsorption, T the evaluated temperature and R_g the universal constant of gases. The optimal Toth parameters, presented in Table 1, were obtained by a nonlinear procedure to give the best fit to the experimental data (the sum of the total average relative error (ARE) [26] at the three evaluated temperatures was taken as the objective function). As can be seen from Fig. 1, this model describes satisfactorily the equilibrium of adsorption of pure CO_2 in the studied range. Parameter t deviates greatly from unity, which indicates that the system CO_2 -carbon is strongly heterogeneous. The product $n_m b$ of Toth model represents the Henry constant, which is usually taken as a measure of the affinity of the adsorbate-adsorbent pair at low pressures; this value is greater for sample NCLK3.

Table 1. Optimal Toth parameters for the adsorption of CO_2 and N_2 on coffee based carbons between 0 and 50°C

Sample	Adsorbate	n_m (mol kg^{-1})	b_0 (kPa^{-1})	t	Q (kJ mol^{-1})
NCLK3	CO_2	15.6034	0.0567	0.3586	28.71
	N_2	2.7182	0.0023	1.0000	15.65
NCHA29	CO_2	6.8286	0.1077	0.4432	34.95
	N_2	1.8466	0.0037	1.0000	16.05

In order to predict the equilibrium of adsorption of binary CO_2/N_2 mixtures, the adsorption isotherms of pure N_2 were measured in the same temperature range as those of CO_2 (see Fig. 3). NCLK3 presents again higher N_2 uptake than NCHA29, due to its greater micropore volume [15]. However, the adsorption capacity of N_2 is, for both samples, nearly one order of magnitude lower than that of CO_2 . This is attributed to the higher quadrupole moment of the CO_2 molecule. The isosteric heat of adsorption of N_2 on the coffee based carbons, calculated from the Clausius-Clapeyron equation, is nearly half that of CO_2 : 15.70 and 16.04 kJ mol^{-1} for NCLK3 and NCHA29, respectively, and remains constant with loading. Toth model was fitted to the experimental data following the same procedure as for CO_2 adsorption (optimal parameters for N_2 adsorption shown in Table 1). The best fit of the Toth equation leads to the Langmuir model ($t=1$: homogeneous system) for N_2 adsorption (see the good agreement between the model and the experimental data in Fig. 3). In the Langmuir isotherm, parameter Q represents the isosteric heat of adsorption, which should be independent of coverage, which is in good agreement with

the results obtained from application of the Clausius-Clapeyron equation. The product $n_m b$ for N_2 adsorption on the carbons is two orders of magnitude lower than that of CO_2 , indicating a much weaker adsorbate-adsorbent interaction.

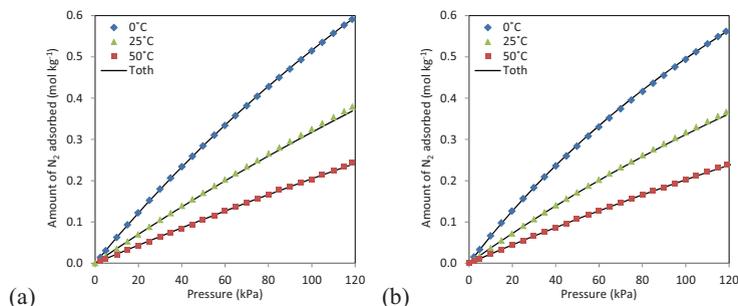


Fig. 3. N_2 adsorption isotherms at 0, 25 and 50°C of samples NCLK3 (a) and NCHA29 (b).

The Ideal Adsorption Solution (IAS) [27] theory was used to predict the binary adsorption equilibrium of CO_2 and N_2 mixtures. MatLab code IAS written by D.D. Do [25] was used to obtain the multicomponent CO_2/N_2 prediction using the pure component Toth model. Fig. 4 compares the binary adsorption isotherms at 25°C and a total pressure of 130 kPa, calculated by the IAS theory, with the pure Toth model for CO_2 and N_2 for the coffee based carbons. The binary adsorption isotherm of N_2 is below that of the pure component while the pure and binary adsorption isotherms of CO_2 are very close to each other. This implies that the presence of N_2 (weak adsorptive) affects little the adsorption capacity of the strong adsorptive, CO_2 , while the presence of CO_2 reduces drastically the adsorption of N_2 in a N_2/CO_2 binary mixture. This behaviour has been reported for highly selective adsorbents, such as zeolite 13X, although it is less pronounced for some activated carbons [22]. Similar results were obtained at 50°C.

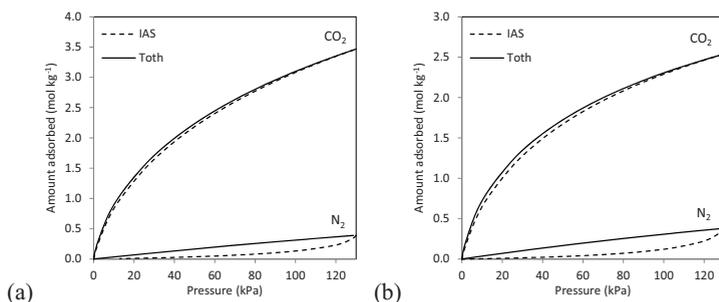


Fig. 4. Pure and binary CO_2 and N_2 adsorption isotherms at 25°C of samples NCLK3 (a) and NCHA29 (b), (solid lines: single Toth model; dashed lines: binary isotherms predicted by IAS Theory).

The equilibrium separation factor for a binary mixture of CO_2 and N_2 is defined by Equation 4 [28], where x refers to the molar fraction in the adsorbed phase and y to the molar fraction in the gas phase. A high separation factor is a key for the screening of adsorbents for a PSA process: the higher the separation factor, the higher product purity is expected [29].

$$S_{1/2} = (x_1/x_2) / (y_1/y_2) \quad (4)$$

Fig. 5 represents the CO₂/N₂ separation factor for the coffee grounds based carbons at a total pressure of 130 kPa and 50°C, conditions that could be found in a postcombustion capture unit. These carbons are highly selective for CO₂ over N₂, especially at low CO₂ partial pressures, which are to be found in the flue gas. According to IAST predictions, sample NCLK3 presents higher selectivity than NCHA29 at a total pressure of 130 kPa and 50°C. Similar results were obtained at 25°C.

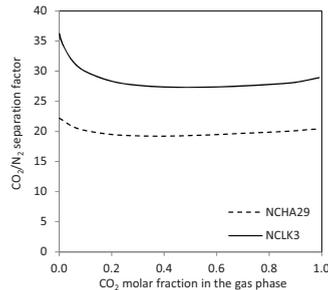


Fig. 5. CO₂/N₂ separation factor at 130 kPa and 50°C of coffee grounds based carbons.

Apart from high selectivity, another important criterion for adsorbent selection in PSA processes is the working capacity (difference between the amount of CO₂ adsorbed at the high pressure adsorption stage and the low pressure evacuation step). This can be preliminarily assessed from the pure equilibrium adsorption data (given that the strong adsorptive is little influenced by the presence of the less adsorptive).

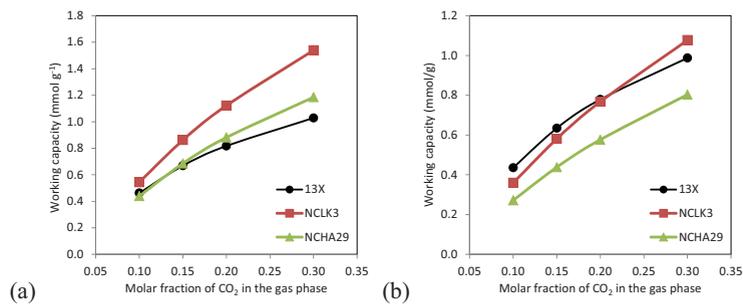


Fig. 6. Estimation of the working capacity from pure CO₂ adsorption on coffee grounds based carbons, NCLK3 and NCHA29, and zeolite 13X (data taken from [23]) at: (a) 20°C; and (b) 40°C, for a feed pressure of 130 kPa and an evacuation pressure of 5 kPa.

Fig. 6 compares the working capacities of the two samples under study with that of zeolite 13X, for a pressure swing adsorption process working between an evacuation pressure of 5 kPa and a feed pressure of 130 kPa at 20 and 40°C, for different CO₂ concentration in the feed gas. Obviously, as the partial pressure of CO₂ in the feed gas approaches the evacuation pressure, the working capacity tends to zero, and conversely, working capacity increases with the partial pressure of CO₂ in the feed gas. Note that

coffee based carbons, especially sample NCLK3, present working capacities comparable or even above that of zeolite 13 X under these conditions. Moreover, heat effects will tend to reduce the working capacity of the adsorbents, and these are expected to be smaller for sample NCLK3, due to its lower isosteric heat of adsorption.

4. Conclusions

Carbons prepared from spent coffee grounds have shown high selectivity for CO₂ over N₂ and a CO₂ working capacity competitive with zeolite 13 X, with the appealing advantage of a significant lower cost. Moreover, carbons are expected to present high stability in moisture conditions and to be easily regenerated by reducing the pressure of the system. Among the carbons under study, NCLK3 showed higher CO₂ adsorption capacity, lower CO₂ isosteric heat of adsorption, and greater CO₂/N₂ selectivity between 0 and 50°C than NCHA29, showing more promising for post-combustion CO₂ capture applications.

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