Green coffee based CO₂ adsorbent with high performance in postcombustion conditions

M.G. Plaza, A.S. González, C. Pevida*, F. Rubiera

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain.

Abstract

An environmentally friendly and low cost adsorbent, PPC (patent application filed [1]), produced from an abundant residue from the food industry, coffee grounds, is presented and evaluated as CO₂ adsorbent in postcombustion conditions. PPC is a high bulk density pelletized carbon with adequate properties for its use in fixed-bed adsorption applications. The equilibrium capacity for CO₂ at low partial pressures, relevant for the postcombustion case, in the 25-50 °C temperature range is superior to that of reference carbons, both in mass and volume basis. PPC presents equilibrium selectivity for CO₂ over N₂, with CO₂/N₂ equilibrium separation factor values of 15-25 at 50 °C and 130 kPa for CO₂ concentrations between 9 and 31 %. Moreover, it presents fast adsorption kinetics, which makes it a good candidate for rapid swing adsorption cycles. Different VSA cycle configurations were carried out at 50 °C in the fixed-bed adsorption unit to evaluate the performance of the adsorbent in cyclic operation. The adsorbent did not show any sign of deactivation over extended operation.

Keywords: CO₂ capture; adsorption; VSA cycles; coffee grounds

1. Introduction

The European Union is committed to an overall greenhouse gas emissions reduction of at least 80 % by 2050. CO₂ capture and storage (CCS) will play an important role in the transition to a low carbon economy, with 7 to 32 % of power generation using CCS by 2050, depending on the scenario considered [2]. CCS involves 3 main routes to continue using fossil fuels in the transition to a low carbon energy system: postcombustion, precombustion and oxyfuel capture. Postcombustion involves the separation of CO₂ from the flue gases generated during combustion. Power stations, oil refineries, petrochemical and gas industries, steel and cement plants are examples of large

* Corresponding author e-mail: cpevida@incar.csic.es

stationary sources that nearly account to half of the CO₂ emissions worldwide, and where this technology could be applied [3]. Chemical absorption with aqueous solutions of alkanolamines is considered the most-ready-to-use technology for postcombustion CO₂ capture. However, it presents a series of drawbacks, like its high energy intensity, mainly associated with the regeneration of the solvent, corrosion issues, large volume of the absorbers due to the required dilution of the corrosive solvent, and amine losses, which negatively affect the environmental impact of the process and the operational cost due to solvent make-up.

Adsorption is a separation technology that can provide substantial energy savings and reduction of the equipment size, as it avoids the need of heating and cooling the large amount of water present in the absorption process. Flue gases are at near atmospheric pressure and present high flow rates, which makes their compression before the separation process uneconomical. Therefore adsorption processes specifically designed for the postcombustion CO₂ capture case should work at a pressure close to atmospheric during the adsorption step. Regeneration can be accomplished at subatmospheric pressures in vacuum swing adsorption (VSA) cycles [4-13], or at approximately constant pressure by temperature swing processes (TSA), in which the bed is regenerated by increasing the temperature of the solid [14-16]. Combinations of both methods (VTSA) to reduce the vacuum and temperature requirements are also possible [17-21]. The design of an optimal adsorption process is a challenging task in which there are many variables that are strongly interrelated (adsorbent properties, feed composition, temperature, cycle configuration, step times, pressure levels, *etc.*), and in which the optimization requires a multiobjective formulation (maximization of purity, recovery and productivity and minimization of energy consumption) [22, 23].

The ideal CO₂ adsorbent should satisfy a series of characteristics: low-cost raw materials, low heat capacity, fast kinetics, high CO₂ adsorption capacity, high CO₂ selectivity, and thermal, chemical and mechanical stability under extensive cycling [24]. Carbon materials obtained from renewable sources satisfy the previous requirements, with the added advantages of global availability, low

environmental impact, low sensitivity to moisture, and easy regeneration, being appealing candidates for this application. The main drawback commonly attributed to carbon adsorbents is their relatively lower adsorption capacity and selectivity compared to other materials. However, the lower affinity towards CO₂ compared to other adsorbents, also makes these materials easier to regenerate, reducing the operating costs of the separation process. Chemical adsorbents present higher selectivity but also require higher energy to be regenerated through TSA processes, which involve longer cycle times. In the case of carbon adsorbents, regeneration can be accomplished by a moderate pressure swing, and the lower working capacity can be overcome by shorter cycles. Moreover, by developing an adsorbent with the adequate pore structure, the adsorption capacity in the conditions of interest can be maximised. In the case of postcombustion capture, where the partial pressure of CO₂ is low, it has been shown that a narrow micropore volume is mandatory [25, 26]. The feasibility of recovering a concentrated CO₂ product from flue gas by a VSA process using activated carbon was first evaluated by simulation in 1993 [27]. Experimental and simulation studies have confirmed these results using different cycle configurations [5, 28, 29]. The use of activated carbons could even avoid the need of a drying step by simultaneous removal of CO₂ and H₂O from flue gas [30, 31].

Our group has explored the potential of different biomass sources as carbon precursors to develop CO₂ adsorbents: sewage sludge, almond shells, olive stones and more recently, coffee grounds [19, 32-39]. The latter is an abundant residue from the food industry: in 2012, 142 million bags of coffee were consumed, which represents an annual average growth rate of 2.4 % over the period 2009-2012 [40], and on average, for each ton of green coffee, 650 kg of spent coffee is generated. Moreover, nearly 50 % of the worldwide coffee produced is processed for soluble coffee preparation, and about 2 kg of wet spent coffee residue is produced for each kg of soluble coffee produced. This residue presents a high organic content, with hemicellulose, proteins, sugars, cellulose, chlorogenic acid, polyphenols, lignin and caffeine as the main constituents [41]. Generally, spent coffee is landfilled, used as fuel in industrial boilers due to its high calorific value [42, 43], or

used for compost production. However, it would be much more desirable to recycle this abundant residue into higher added value products. For example, the bio-components present in the spent coffee could be extracted to be used as ingredients or additives in the food industry due to their antioxidant properties and high nutritional value, or for biodiesel production [44]. The resulting solid by-product could be exploited as a precursor for developing carbon materials [45]. Carbon adsorbents can be produced from coffee waste by chemical activation with zinc chloride [46, 47], phosphoric acid [48], mixtures of zinc chloride and phosphoric acid [49], potassium hydroxide [38, 50], or by physical activation with CO_2 [38, 46, 51], H_2O [46] or air [52]. The carbons produced from spent coffee have shown to be suitable for the adsorption of organic pollutants and dyes from waste waters [46, 48, 49, 52], but also for gas phase applications, such as H_2S separation [48], natural gas storage [48], or CO_2 capture [38, 53].

In previous works from our group [38, 53], the development of microporous carbon adsorbents with potential use as CO_2 adsorbents was explored through physical and chemical activation of spent coffee grounds. The coffee-based carbons were evaluated in terms of texture development and CO_2 adsorption measurements were carried out in a volumetric and a thermogravimetric apparatus. However, the fine particle size of these powdered activated carbons (PAC) impeded the evaluation of the adsorbents at a higher scale, using a fixed bed adsorption unit. In this work, the previous limitation was overcome by producing the adsorbent directly in pellet form. The potential for the application of this adsorbent to separate CO_2 from the main flue gas component, N_2 , was first assessed by studying the equilibrium of adsorption of these two adsorbates at 0, 25 and 50 °C. The kinetics of adsorption were then evaluated through dynamic adsorption experiments using a single pellet, and by fixed-bed breakthrough experiments carried out in an adsorption unit using binary N_2/CO_2 gas mixtures with different CO_2 concentration representative of postcombustion conditions. Finally, a series of vacuum swing adsorption (VSA) configurations were evaluated experimentally in the fixed-bed adsorption unit at 50 °C to evaluate the performance of the adsorbent in cyclic operation.

2. Materials and methods

2.1. Adsorbent preparation and characterization

A solid coffee residue recovered from spent Nespresso® capsules was used as the starting material. Prior to any ulterior treatment, the residue was air-dried at 100 °C for 4 h to remove the excess water. The spent coffee grounds, which present a fine particle size (90 % by weight is below 425 μm), were shaped into pellets with a diameter of 4 mm and a height of 3 mm using a single stamping tablet machine. No binder was added during the conformation process.

The shaped coffee residue was activated in a single stage, using CO_2 as the activating agent. The activation temperature and soaking time were optimized to maximize the micropore volume and CO_2 adsorption capacity of the final carbons. Here only the results for carbon PPC (patent application filed [1]) are shown. The activated product preserves the cylindrical shape of the precursor, with an average diameter of 2.67 ± 0.05 mm and a height of 1.88 ± 0.13 mm (based on the measured dimensions of 10 pellets). The carbon yield (g of final carbon adsorbent per 100 g of dry coffee grounds) is 22 %, which is relatively high for a biomass precursor.

The ultimate analysis of PPC is shown in Table 1. The carbon, hydrogen and nitrogen content were determined using a LECO CHN-2000 and the oxygen content in a LECO VTF-900.

The porous texture of PPC was assessed from the adsorption isotherms of N_2 at -196 °C and CO_2 at 0 °C. These were obtained in a TriStar 3000 apparatus from Micromeritics. The total pore volume, V_p , was estimated from the amount of N_2 adsorbed at a relative pressure of 0.99, and the micropore volume, V_{DR} , was calculated from the Dubinin-Radushkevitch method [54]. The BET surface area is also shown in Table 1 for comparative purposes. The distribution of the narrow microporosity was assessed by Density Functional Theory applied to the adsorption isotherm of CO_2 at 0 °C assuming slit pore geometry, non-negative regularization and little smoothing, using Micromeritics' software. Table 1 also shows the solid, particle and bulk densities of PPC. The solid density (ρ_s) was estimated by helium picnometry at 35 °C using an AccuPyc 1330 from Micromeritics. The particle density (ρ_p) was calculated from the dry mass and volume of single PPC pellets (the value given in Table 1 is the

average value for 10 pellets). The apparent density was determined by mercury intrusion at 0.1 MPa using an Autopore IV 9500 from Micromeritics, for comparison purposes with materials of irregular shape. The bulk density of PPC was measured in the fixed bed adsorber used to carry out the dynamic adsorption experiments, and also by an automatic tapped density analyser Autotap from Quantachrome, using a graduated cylinder of 10 cc.

Table 1. Adsorbent properties

Ultimate analysis (wt. % dry ash free basis)		C	85.1
		H	1.2
		N	4.7
		O	9.0
Textural characterisation	N ₂ adsorption at -196 °C	V _p (cc g ⁻¹)	0.21
		V _{DR-N2} (cc g ⁻¹)	0.21
		S _{BET} (m ² g ⁻¹)	522
	CO ₂ adsorption at 0 °C	V _{DR-CO2} (cc g ⁻¹)	0.23
	Density	ρ _s (kg m ⁻³)	1850 ^a
		ρ _p (kg m ⁻³)	766 ^b /743 ^c
		ρ _b (kg m ⁻³)	373 ^d /421 ^e

^aDetermined by helium picnometry at 35 °C; ^bAverage particle density determined from the volume and dry mass of 10 individual pellets; ^cDetermined by mercury intrusion at 0.1 MPa; ^dBed density of the fixed-bed adsorption unit used to carry out the dynamic experiments; ^eDetermined using an automatic tapped density analyser with a 10 cc graduated cylinder.

2.2. Equilibrium of adsorption

2.2.1. Pure components

The equilibrium of adsorption of the single components was assessed from the adsorption isotherms of CO₂ and N₂ at 0, 25 and 50 °C. These isotherms were obtained in a TriStar 3000 apparatus from Micromeritics.

Pure component adsorption isotherms were fitted to the Toth adsorption model:

$$\frac{q}{q_s} = \frac{K P^t}{1 + K P^t} \quad (1)$$

where q is the saturation capacity, K is the affinity constant, P is the pressure and t is a parameter that characterises the heterogeneity of the system (usually less than unity). The affinity constant was assumed to present the following temperature dependence [55]:

$$K = K_0 \exp\left(\frac{Q}{RT}\right) \quad (2)$$

where K_0 is the affinity constant at a reference temperature (T_0) (here taken as 0 °C), R is the universal constant of gases, and Q is a fitting parameter related to the heat of adsorption, as it will be discussed later.

The heterogeneity parameter, t , was assumed to take the following empirical functional form of temperature dependence [55]:

$$t = \alpha \exp\left(\frac{Q}{RT}\right) \quad (3)$$

Parameters K_0 , Q , α and α were fitted to minimise the sum of square residuals (SQR) between the experimental data and the model prediction:

$$SQR = \sum_{i=1}^N (q_i - q_{calc,i})^2 \quad (4)$$

where N refers to the number of data points measured at each temperature T , and q_i and $q_{calc,i}$ refer to the amounts adsorbed at a pressure P and a temperature T , measured experimentally and calculated by the model, respectively.

The isosteric heat of adsorption (Q_{st}) was estimated from the adsorption isotherms by plotting $\ln P$ versus $1/T$ at constant adsorbed amounts (isosteres), which yield to straight lines with slope equal to: $-Q_{st}/R$. Isosteres were obtained by linear interpolation of the experimental adsorption data at 0, 25 and 50 °C using Matlab software. This approach implicitly assumes that the heat of adsorption is independent of temperature in the range evaluated, which is corroborated by the linearity of the plot. A second approach to obtain the isosteric heat of adsorption from the experimental adsorption isotherms is to apply the van't Hoff equation to an adsorption model that represents the equilibrium

data. Using the temperature dependent Toth model to describe the equilibrium of adsorption, the isosteric heat of adsorption is given by [55]:

$$\frac{d \ln p}{d \ln V} = \frac{E_a}{RT^2} \quad (5)$$

2.2.2. Binary equilibrium

The pure component Toth model was used to predict the equilibrium of adsorption of binary N₂/CO₂ mixtures through the Ideal Adsorption Solution (IAS) theory, making use of the Matlab program written by D.D. Do [55]. This entails to calculate the amount of each species adsorbed from a multicomponent gas mixture of known composition and pressure. Values given by IAS were compared with the results from the fixed-bed adsorption experiments carried out with binary N₂/CO₂ mixtures.

2.3. Dynamic adsorption experiments with binary N₂/CO₂ mixtures

2.3.1. Single pellet adsorption experiments in TGA

The influence of intraparticle mass transfer resistance on the adsorption kinetics of a single pellet was evaluated using a thermogravimetric analyser TGA/DSC1 STAR[®] System from Mettler Toledo. The test consisted of an initial drying step carried out at 100 °C in 100 sccm¹ of nitrogen, followed by cooling down to 50 °C in N₂ flow; subsequently, at time zero, the feed gas was changed from pure N₂ to a mixture with 10 % of CO₂ and 90 % N₂. Buoyancy and drag effects were corrected by subtracting a blank experiment. The adsorption process was monitored by the mass gain experienced by the pellet.

2.3.2. Fixed-bed adsorption experiments

Breakthrough experiments and VSA cycles were carried out with binary N₂/CO₂ mixtures in a fixed bed adsorption unit (Figure 1). The adsorber consists of a stainless steel column (I.D. = 9.12 mm)

¹ sccm is the abbreviation of standard cubic centimeter per minute (cm³ min⁻¹ at 0 °C and 101.325 kPa)

placed in vertical position with a porous plate in its base (maximum adsorbent height of *ca.* 150 mm) and equipped with temperature and pressure control. The column was carefully filled with 3.5 g of PPC manually tapping the column during the process. The bulk density of the bed was measured before and after running the breakthrough experiments and VSA cycles, with coincident results, indicating that the adsorbent did not suffer noticeable attrition. The small void space above the solid surface was filled with glass wool to reduce the dead volume and facilitate the uniform distribution of the feed in the adsorber section.

The feed gas is composed by the mixture of individual streams of N₂, CO₂ and He, which flow rate is set by accurate mass flow controllers. These are mixed in a helicoidal distributor prior to enter the adsorber column at the upper end. A K-type thermocouple placed in the bulk of the adsorbent bed, near the feed entrance, allows monitoring the temperature of the adsorbent (± 1 °C). Pressure is registered by means of a pressure sensor (-1-40 barg) located in the effluent line. Vacuum can be automatically applied at the adsorber outlet through a 3-way pneumatic valve. The vacuum line is composed by a vacuum controller coupled to a Pirani transmitter and an electromagnetic angle valve that is connected to a diaphragm pump. The composition of the effluent gas is analysed by a dual channel Micro Gas Chromatograph CP-4900 from Varian. A constant flow rate of oxygen (not present in the feed mixture) was added before the analysis section by means of a fourth mass flow controller to determine the flow rate of the effluent stream. It is important to determine the flow rate and not only the gas composition of the effluent, as its flow rate varies during the adsorption step (this variation is not negligible in bulk separations), and especially during VSA cycles, where great changes in the flow rates occur during the depressurization step. Back mixing is prevented by a rational distribution of check valves within the experimental set up (see Figure 1).

Figure 1. Scheme of the fixed-bed adsorption unit.

The amount of N_2 and CO_2 adsorbed at equilibrium was estimated from the breakthrough experiments by making a component mass balance to the adsorber and discounting the hold up in the gas phase (void volume of the unit and total porosity of the bed):

$$\frac{dQ}{dt} = \frac{F_{i,0} - F_{i,t}}{W} \quad (6)$$

Where Q is the amount of species i adsorbed at a time t at which the adsorbent has reached equilibrium (Q_0 , Q is the amount of species i adsorbed at $t=0$, $F_{i,0}$ is the molar flow rate of the species i fed to the adsorber, $F_{i,t}$ is the molar flow rate of the species i leaving the adsorber, V_d is the dead volume of the unit, R_g is the universal constant of gases, T is the temperature of the unit, $P_{i,t}$ is the partial pressure of the species i in the gas phase at time t , $P_{i,0}$ is the partial pressure of the species i in the gas phase at $t=0$, ϵ is the total void fraction of the bed (it includes the intraparticle and interparticle porosity), V_b is the bed volume, T_b is the temperature of the bed, and W is the dry mass of adsorbent used.

Any VSA cycle can be considered as a series of elementary steps; the processes differ in the sequence of these elementary steps and in the way that they are carried out. Three parameters are usually calculated to compare different cycle configurations and adsorbent performance: the purity of CO₂ in the product stream, the recovery of CO₂ and the CO₂ throughput per mass of adsorbent and cycle time. These parameters were calculated as follows:

$$\frac{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt}{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt + \int_{t_{p+1}}^{t_{p+2}} Q_{CO_2} dt} \quad (7)$$

$$\frac{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt}{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt + \int_{t_{p+1}}^{t_{p+2}} Q_{CO_2} dt} \quad (8)$$

$$\frac{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt}{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt + \int_{t_{p+1}}^{t_{p+2}} Q_{CO_2} dt} \quad (9)$$

Where t_p refers to the time of the cycle at which the production step begins, t_{p+1} refers to the cycle time at which the production step is finalised, and t_{p+2} to the full cycle time. To reduce the calculation error in the integration of the outlet flow rate due to the limited number of data points, the information of several cycles at the cyclic steady state was used (CSS). CSS is attained when the molar flow rates at any time in the cycle remain the same in all subsequent cycles. The validity of the calculation method was checked by doing a partial mass balance to CO₂ and N₂ over the whole cycle time at CSS:

$$0.$$

Alternatively, when the VSA cycle configuration includes a step with product recycle (rinse) the recovery and productivity of CO₂ are sometimes calculated by:

$$\frac{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt}{\int_{t_p}^{t_{p+1}} Q_{CO_2} dt + \int_{t_{p+1}}^{t_{p+2}} Q_{CO_2} dt} \quad (10)$$

where $t_{f,Rinse}$ refers to the cycle time at which the rinse step begins, and $t_{f,Rinse}$ to the cycle time at which the rinse step finishes.

3. Results and discussion

3.1 Characterization of PPC

Carbon PPC presents a relatively high oxygen and nitrogen content (Table 1) that comes from the precursor [38]. Although the spent coffee grounds have an acidic surface ($pH_{PZC} = 5.2$), the carbons obtained by physical activation with CO_2 present basic character ($pH_{PZC} \approx 10$) [38], which implies that the nitrogen and oxygen moieties present in the activated samples must be forming part of thermally stable and basic functionalities like pyrones and pyridines. The CO_2 adsorption performance of a porous carbon is mainly governed by its pore size distribution and the operation conditions (temperature and pressure) [25, 26]. However, the surface chemistry can also play a role: the presence of surface N and O donor groups can enhance the adsorbent-adsorbate interactions, favouring CO_2 selectivity and adsorption capacity [19, 56-58]. The inorganic matter naturally present in biomass-derived activated carbons, mainly K compounds, have also shown to present a positive effect on the adsorption of CO_2 [59]. The metals present in CO_2 -activated coffee carbons are Ca, Al, K, Si, P, Mg, Fe and Na [38, 60].

Figure 2 shows the N_2 adsorption isotherm of carbon PPC. It is a Type I isotherm, with a horizontal plateau, and without hysteresis loop, which is characteristic of strictly microporous solids. In fact, the total pore volume, $0.21 \text{ cm}^3 \text{ g}^{-1}$, is equal to the micropore volume determined by the Dubinin-Radushkevitch applied to the N_2 adsorption isotherm. Although the BET surface area of this material presents a moderate value (see Table 1), the shape of the N_2 adsorption isotherm reflects a narrow pore size distribution in the micropore domain, which is highly desirable for the adsorption of CO_2 at

low partial pressures (postcombustion case) [19, 25, 26]. The micropore volume and BET surface area of PPC are close to those previously obtained from unshaped spent coffee grounds by physical activation following a two-step activation procedure (carbonisation in N_2 followed by activation with CO_2), but lower than those obtained by KOH activation [38]. However, PPC presents the added advantages of a greater particle size, that allows its used in fixed-bed operations, and a greater carbon yield (22 wt.% vs. 7-16 wt.% [38]). Moreover, compared to the chemical activation route, activation with CO_2 presents a lower environmental impact.

Figure 2. N_2 adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ on PPC.

The adsorption isotherm of CO_2 at $0\text{ }^{\circ}\text{C}$ is commonly used to assess the narrow micropores ($<1\text{ nm}$). The DR method applied to the adsorption isotherm of CO_2 leads to a slightly higher micropore volume ($0.23\text{ cm}^3\text{ g}^{-1}$) than that determined from N_2 adsorption ($0.21\text{ cm}^3\text{ g}^{-1}$). Figure 3 represents the micropore size distribution obtained from the CO_2 adsorption isotherm by DFT. As shown in the figure, most of the micropores present a pore size between 0.35 and 0.65 nm , which is highly desirable for postcombustion CO_2 capture applications [25, 26].

Figure 3. Pore size distribution of the narrow micropores calculated from the CO₂ adsorption isotherm at 0 °C by DFT assuming slit pore geometry (non-negative regularization and little smoothing applied).

As can be seen in Table 2, the apparent density of PPC is high compared to other biomass-based granular activated carbons (GAC), like Norit C GRAN, which is a commercial GAC obtained from wood by a phosphoric acid activation route, or OS and AS, which are GAC prepared in our laboratory facilities from olive stones and almond shells, respectively, by the same activation route as PPC [61].

Table 2 . Comparison of the apparent and bulk density of different carbon adsorbents

Sample	Type	Precursor	Apparent density ^a (kg m ⁻³)	Bulk density (kg m ⁻³)
PPC	Pellet	Coffee grounds	743	421 ^b
Norit C GRAN	GAC	Wood	400	218 ^b / 230 ^c
Norit R2030 CO2 [18]	Extrudate	Peat	850	476 ^b / 560 ^c
Calgon BPL® 4x6	GAC	Coal	NA	430 ^c
OS [61]	GAC	Olive stones	536	314 ^b
AS [61]	GAC	Almond shells	517	232 ^b

^a Determined by mercury intrusion at 0.1 MPa; ^b Bulk tapped density measured in a 10 cc graduated cylinder;

^c Data given by manufacturer

The bulk density of PPC is also higher than those of the aforementioned biomass-based GAC, and even close to other type of commercial activated carbons, as can be seen in Table 2. BPL is a

bituminous coal-based GAC extensively used for gas phase applications, and Norit R2030 CO₂ is a peat-based extruded carbon commercialised for CO₂ adsorption in cold storage ware houses. The bulk density is an important factor, as it determines the volume of the adsorber required for a specific application.

3.2 Equilibrium of adsorption of pure components

The adsorption isotherms of CO₂ at 0, 25 and 50 °C up to 120 kPa are shown in

Figure 4. As expected for a physisorption process, the adsorbed amount increases with increasing pressure at a given temperature and decreases with increasing temperature at a given pressure. As shown in the figure, CO₂ adsorption can be adequately described by the relative simple Toth model in the pressure and temperature range evaluated.

Figure 4. CO₂ adsorption isotherms at 0, 25 and 50 °C on PPC.

The adsorption capacity of CO₂ at low partial pressures is higher than that of commercial carbon adsorbents BPL and Norit R 2030 CO₂, as can be seen in Table 3. The CO₂ adsorption capacity is shown in mass basis (mol kg⁻¹) which are the units obtained from the adsorption isotherm measurements, and in volumetric basis (mol m⁻³), which was calculated from the prior amount by

making use of the bulk density of the materials. The adsorption capacity of CO₂ on PPC is also higher than that of the GAC obtained by the same activation route from different biomass residues: OS and AS, especially in volume basis, due to its greater bulk density.

Table 3. Comparison of the CO₂ adsorption capacity of different carbon materials
CO₂ adsorption capacity at 15 kPa

Sample	(mmol g ⁻¹)		(mol m ⁻³)	
	25 °C	50 °C	25 °C	50 °C
PPC	1.2	0.7	509 ^a	337 ^a
Norit R2030 CO2	0.8	0.5	398 ^a -468 ^b	225 ^a -265 ^b
BPL	0.7 [4]	0.4 [4]	300 ^b	186 ^b
OS	1.0 [61]	0.6 [61]	320 ^a	181 ^a
AS	1.1 [61]	0.7 [61]	250 ^a	156 ^a

^a Calculated using the bulk tapped density determined in a 10 cc graduated cylinder; ^b Calculated using the bulk density data provided by the manufacturer

One of the advantages of carbon materials when compared to other type of adsorbents is that they are easier to regenerate. This is reflected in the shape of the adsorption isotherms of CO₂, which are not excessively steep, facilitating regeneration by pressure reduction in a VSA process. Other adsorbents (e.g. zeolite 13X) present higher adsorption capacities but also steeper isotherms, thus requiring higher pressure ratios to achieve high working capacities. For a moderate pressure ratio (highly desirable from an economical point of view), similar CO₂ working capacities can be obtained using carbon adsorbents and zeolites [53].

The adsorption isotherms of N₂ at 0, 25 and 50 °C up to 120 kPa are shown in Figure 5. They present a nearly linear topology, due to the weak dispersion forces existent between the N₂ molecule and the carbon surface. N₂ adsorption capacity is substantially smaller than that of CO₂ at the same temperature and pressure: the ratio of the adsorption capacity of CO₂ over that of N₂ increases with

increasing temperature and decreasing pressure, from 6-9 at 1 bar to 18-24 at 0.1 bar in the 0-50 °C temperature range. As can be seen from the figure, the Toth model also results adequate to describe the adsorption behaviour of N₂ in the temperature and pressure range evaluated.

Figure 5. N₂ adsorption isotherms at 0, 25 and 50 °C on PPC.

Fitted parameters of the Toth model for the adsorption of N₂ and CO₂ in the pressure and temperature range evaluated can be found in Table 4. Parameter t deviates more from unity in the case of CO₂ adsorption, indicating a stronger degree of heterogeneity for the CO₂-carbon system. The value of t increases with temperature ($\alpha > 0$), because the isotherms tend to be less favourable as temperature increases. In fact, t approaches unity for the adsorption of N₂ at 50 °C (Toth reduces to Langmuir model, which assumes homogeneous adsorption sites). Parameter Q , which represents the heat of adsorption at zero loading, according to Equation 5, is 2.5 times higher for CO₂ than for N₂, in good agreement with the lesser affinity for the latter adsorbate.

Table 4. Optimal parameters of the Toth model for the adsorption of CO₂ and N₂ on PPC carbon

	Toth	
	CO ₂	N ₂
$C_{\mu s}$ (mol kg ⁻¹)	21.368	3.678
b_0 (kPa ⁻¹)	0.3176	0.0023
t_0	0.217	0.704
α	0.341	1.912
Q (kJ mol ⁻¹)	46.482	18.442

Figure 6 compares the values of the isosteric heat of adsorption obtained from the slope of the isosteres in the 0 -50 °C range (symbols) with that given by the Toth model (lines). The isosteric heat of adsorption presents a decreasing trend with the amount of CO₂ adsorbed, as expected for heterogeneous systems, in which the adsorption sites of higher energy are preferentially occupied at the lower pressures and the lower energy sites are progressively occupied as pressure (or loading) increases. The isosteres show linear pattern between 0 and 50 °C, although the correlation coefficient increases with increasing loading (see supporting information). In Figure 6 only the data from the isosteres that presented a correlation coefficient above 0.99 in the 0-50 °C range have been included (> 0.7 mmol g⁻¹). At low loadings (< 0.4 mmol g⁻¹) the slope of the isosteres calculated using the data at 0, 25 and 50 °C predicts an unexpected increasing trend of the isosteric heat of adsorption with the adsorbed amount; in this region the correlation coefficient falls below 0.95, which indicates that temperature dependence of q_{st} is not negligible in the temperature range of 0-50 °C. The Toth model predicts the dependence of the isosteric heat of adsorption with temperature and with the amount of CO₂ adsorbed. The values obtained from the slope of the isosteres using the equilibrium data at 0, 25 and 50 °C match with the prediction of the Toth model at the intermediate temperature (25 °C). A moderate value of the isosteric heat of adsorption is

desired, as this will facilitate the regeneration of the adsorbent and reduce the heat effects during cyclic operation.

Figure 6. Isosteric heat of adsorption of CO₂ as a function of loading, calculated from the slope of the isosteres in the temperature range between 0 and 50 °C (symbols) and using Equation 5 (lines).

3.3. Dynamic adsorption experiments with binary N₂/CO₂ mixtures

3.3.1. Single pellet uptake measurements

The rate of physical adsorption is generally controlled by diffusional limitations rather than by the equilibrium of adsorption, which is normally very rapid [62]. Adsorption takes place at the solid surface, so the adsorbate must diffuse first through the external fluid film surrounding the pellet and then through the pore volume. To assess the diffusional resistance in PPC, a single pellet was subjected to a step change in concentration (from 100 % N₂ to 90 % N₂ + 10 % CO₂) at 50 °C. Figure 7 compares the fractional mass uptake of a single pellet of PPC (1 pellet) with that of a pellet cut in two by the axial dimension (1/2 pellet). Intraparticle diffusion becomes more significant at the initial stages of the uptake, when adsorption occurs at the outside of the particle. However, the differences observed between the uptakes curves of the two pellets with different size are small, which indicates that diffusional resistance inside the particle is not controlling the overall rate of mass uptake. A reduced mass transfer resistance is highly desirable to maximise throughput in rapid swing adsorption cycles.

Figure 7. Effect of pellet size in the fractional mass uptake experienced by a single pellet in 100 sccm flow rate of a binary mixture with 10 % CO_2 (balance N_2) at 50°C .

3.3.2. Breakthrough experiments

A series of breakthrough curves were obtained at 50°C , which is a feasible operation temperature for a postcombustion unit, using binary mixtures of CO_2 and N_2 . The concentration of CO_2 in the feed mixture was varied between 9 and 31 % to cover the concentration range of CO_2 in the different streams that can be encountered in postcombustion applications: natural gas fired boilers (7-10 %), oil fired boilers (11-13 %), coal fired boilers (12-14 %), oil refinery and petrochemical plant fired heaters (8 %), blast furnace gas (20-27 %), cement kiln off-gas (14-33 %), syngas after gasification, *etc.* [3].

Figure 8 represents six consecutive breakthrough curves (BC 1-6) carried out with a feed consisting of 61 sccm with 31 % CO_2 (balance N_2) at 130 kPa and 50°C . The lines represent the molar flow rates of N_2 (blue) and CO_2 (red) fed to the adsorber, and the symbols represent the molar flow rates of N_2 (diamonds) and CO_2 (circles) leaving the adsorber. Symbols overlap for all the consecutive BC, indicating a good repeatability and reproducibility of the results. The least strongly adsorbed species, N_2 , passes more rapidly through the column, emerging with a sharp profile (Figure 8a). The molar flow rate of N_2 in the effluent goes through a first maximum that simply mimics the dynamic behaviour of the feed flow rate (opening and regulation of the mass flow controller valve). However,

in the time interval between 2.2 and 6.2 min the molar flow rate of N_2 in the effluent is higher than that of the feed, due to the displacement of adsorbed N_2 by the preferential adsorption of the slower moving CO_2 . During a time lapse of approximately 5 min, a decarbonised effluent leaves the adsorber. When the CO_2 adsorption front reaches the adsorber outlet, the molar flow rate of CO_2 in the effluent increases rapidly and the molar flow rate of N_2 decreases both tending to the feed values.

The adsorbent was regenerated with helium at 150 °C between consecutive breakthrough curves (see Figure 8b). N_2 leaves the adsorber more readily than CO_2 : the molar flow rates go through a maximum at around 10 s for N_2 and 70 s for CO_2 from the beginning of the desorption step. Temperature was raised during the regeneration step to facilitate desorption, ensuring full regeneration of the adsorbent and repeatability of consecutive breakthrough curves. Although it is not necessary to raise temperature for CO_2 to desorb, regeneration can be accomplished in a shorter time if the temperature of the adsorbent is increased.

Figure 8. (a) Binary N_2/CO_2 breakthrough curves carried out at 130 kPa and 50 °C departing from a bed initially full of helium using a feed with 31 % CO_2 (balance N_2); (b) Desorption of CO_2 and N_2 during the regeneration step in helium flow at 130 kPa.

Similar results were obtained at lower concentrations of CO_2 in the feed stream. Figure 9 compares the breakthrough curves for CO_2 obtained by varying the concentration of CO_2 in the feed while keeping constant the total feed flow rate. The curves become steeper as the CO_2 concentration of the gas phase increases. This can be explained by the increase in the driving force for adsorption. For example, in the solid film linear rate approximation, the rate of adsorption is given by [62]:

(12)

where k_i is the linear driving force constant for the species i , q_i is the adsorption capacity at equilibrium and q the amount adsorbed. The driving force for CO₂ adsorption in a breakthrough experiment where the adsorbent is initially free of adsorbate, is maximum at $t=0$ ($q=0$), and increases with the partial pressure of CO₂ in the gas phase: P_{CO_2} . The sharpness of the curves indicates that the overall mass transfer resistance is small, which is highly desirable for rapid swing adsorption processes.

Figure 9. Effect of feed concentration on the CO₂ breakthrough curves carried out with a feed flow rate of 61 sccm at a temperature of 50 °C and a total pressure of 130 kPa.

Figure 10 represents a comparison of two breakthrough experiments carried out with a feed of similar composition (16 % CO₂, balance N₂) but using different flow rates: 34 and 71 sccm. The CO₂ breakthrough curves are represented *versus* an adimensional time, defined by: $\tau = t/t_{st}$, where t_{st} is the stoichiometric time, calculated by Equation 12.

(13)

Figure 10. Effect of feed flow rate on the CO₂ breakthrough curves carried out at a temperature of 50 °C and a total pressure of 130 kPa for a feed with 16 % CO₂ (balance N₂).

The main effect of increasing the feed flow rate is the reduction of the stoichiometric time from 10.7 min to 5.5 min. On the other hand, the feed flow rate has little effect on the shape of the breakthrough curve (see Figure 10), which implies that the axial dispersion and the external fluid film resistance, which are affected by the gas velocity, are not controlling the overall rate of the adsorption process. Axial mixing is undesirable, as it reduces the efficiency of the separation [62]. It can arise from wall effects, non-uniform packing, molecular diffusion and turbulent mixing. To minimize axial dispersion, the bed should be packed carefully, and the gas velocity should be kept high [62]. The Peclet number is commonly used to quantify the degree of axial dispersion. This adimensional number, can be defined for the column as: $Pe = \frac{u H_b}{E_z}$, where u is the gas velocity, H_b is the height of the adsorbent bed and E_z is an axial dispersion coefficient, that has been estimated by the following correlation:

$$E_z = \frac{D_{mi}}{R_p} \left(\frac{1 - \epsilon_p}{\epsilon_p} \right) \quad (13)$$

where D_{mi} is the molecular diffusivity of species i in the gas mixture, R_p is the particle radius, and ϵ_p is the interparticle porosity. The molecular diffusivities in the binary mixture were calculated by the

Chapman-Enskog Equation [63]. In the experimental conditions evaluated the Peclet number is around 80, which confirms the low contribution of axial dispersion (values below 30 are taken as indicative of significant contribution of axial dispersion, and above 100 of near plug flow conditions). The amount of N_2 and CO_2 adsorbed from the binary mixtures was estimated from the experimental breakthrough experiments by making a component mass balance to the adsorber and discounting the hold up in the gas phase (Equation 6). To reduce the error associated to semicontinuous analysis, the data of six consecutive runs was used for the integration. Values presented in Figure 11 correspond to the average for the adsorption and desorption experiments; these fall in the range between 0.5 and 1.1 mmol g^{-1} for CO_2 and 0.2-0.3 mmol g^{-1} for N_2 in the experimental conditions evaluated: 130 kPa and 50 °C and CO_2 concentration between 9 and 31 % (N_2 balance) .

Figure 11 compares the calculated amount of CO_2 and N_2 adsorbed during the binary breakthrough curves with the prediction given by the Ideal Adsorption Solution Theory (IAST) for binary CO_2/N_2 mixtures with CO_2 concentrations ranging from 0 to 100 % at a temperature of 50 °C and a total pressure of 130 kPa. IAS theory predicts a decrease in the adsorption capacity of N_2 (weak adsorbate) in the presence of CO_2 (strong adsorbate) by 32-49 % compared to the pure component Toth model in the concentration range evaluated experimentally (9-31 % CO_2), and a reduction in the adsorption capacity of CO_2 of only 2-5 % (the Toth model for the adsorption of the single components has been included in Figure 11 for comparison purposes). The trend of the amount of N_2 adsorbed with partial pressure, estimated from the binary breakthrough experiments, presents greater dispersion than that of CO_2 due to the inherent limitations of the calculation method. Moreover, as the adsorption capacity of N_2 is significantly lower than that of CO_2 , small absolute differences are translated in greater relative error. According to the experimental results, IAST subestimates the amount of N_2 coadsorbed with CO_2 by 7-42 %, while it slightly overestimates the adsorption of CO_2 by 2-8%.

Figure 11. Comparison of the amount of CO₂ and N₂ adsorbed calculated from experimental breakthrough experiments with the single component prediction (Toth model) and the prediction for the binary mixture using the IAS theory.

In adsorption separation processes it is common to define an equilibrium separation factor by:

$$\alpha = \frac{y_1}{y_2} \frac{x_2}{x_1} \quad (8)$$

where x refers to the molar fraction of the adsorbed phase and y to that of the gas phase. The value of the separation factor varies with the experimental conditions: composition of the gas phase, temperature and pressure. Moreover, the values calculated from experimental results are very sensible to the uncertainty associated to the calculation of the amount adsorbed. Figure 12 compares the values of α calculated from the binary breakthrough experiments with the predictions obtained using the Toth model for the single components and that obtained making use of the IAS theory. IAST predicts a decrease of the CO₂/N₂ separation factor as the concentration of CO₂ in the gas phase increases, from values of 35 for mixtures containing 3 % CO₂ to values of 23 for mixtures with 40 % CO₂ at an adsorption temperature of 50 °C and a total pressure of 130 kPa. The experimental results lead to values of the separation factor between 15 and 25 for CO₂ concentration between 9 and 31 % at 50 °C and 130 kPa. These values are below those given by the IAST prediction, and closer to those calculated using the Toth model for the pure components, due to the underestimation of the amount of N₂ coadsorbed with CO₂ by IAST. In any case, the

experimental values are well above unity, which implies that PPC is a good adsorbent to carry out CO_2/N_2 separations in postcombustion conditions.

Figure 12. CO_2/N_2 equilibrium separation factor of the coffee based carbon at 50 °C and 130 kPa as a function of CO_2 molar fraction in the gas phase.

A breakthrough experiment was carried out with 101 sccm (16 % CO_2 , balance N_2) at room temperature (21 °C) and 130 kPa, without temperature control, to observe the magnitude of the temperature rise due to the adsorption process. A K-type thermocouple, placed in the bulk of the adsorbent, at near 3.5 cm from the feed end, monitored the temperature during the adsorption process. Results are shown in Figure 13. The adsorber was initially full of N_2 at 21 °C and 130 kPa. As in the previous cases, at the beginning of the breakthrough experiment, practically all the incoming CO_2 is adsorbed, producing a decarbonized effluent throughout 6 min. The temperature of the adsorbent bed, initially in equilibrium at 21 °C, starts to increase after 1.3 min, reaching a maximum temperature of 27 °C as a consequence of the exothermic adsorption of CO_2 . Subsequently, the temperature starts to decrease again due to heat dissipation to the ambient air through the column wall (the adsorption column was not thermally insulated), recovering the equilibrium temperature, 21 °C, in only 9 min. This temperature shift is small, which is highly

desirable, as a large temperature rise of the solid during adsorption reduces the adsorption capacity of the solid.

Figure 13. CO₂ breakthrough curve carried out at room temperature and a total pressure of 130 kPa with a feed consisting on 101 sccm with 16 %CO₂ (balance N₂).

The amount of CO₂ and N₂ adsorbed at equilibrium with the binary feed, calculated from the breakthrough curves using Equation 6, is 1.3 mmol g⁻¹ and 0.3 mmol g⁻¹, respectively, which falls between the prediction of the Toth model for the pure components at 21 °C and that given by IAST for the adsorption from a mixture with 16 % CO₂ (balance N₂) at 21 °C and a total pressure of 130 kPa. IAST underestimates the amount of N₂ adsorbed by 74 % and that of CO₂ by 4 %, while the adsorption capacities expected for the pure components at the same partial pressures, given by the Toth model, are 13 and 11 % higher than the experimental values for CO₂ and for N₂, respectively. The experimental CO₂/N₂ equilibrium separation factor is 27, which is higher than that observed at 50 °C. The experimental value is again closer to the value predicted by the pure component Toth model (28) than to that determined by IAST (46), due to the underestimation of the amount of N₂ adsorbed by IAST.

3.3.3. Vacuum Swing Adsorption cycles

A series of VSA cycles were carried out in the one-column adsorption unit used to carry out the breakthrough curves (Figure 1). The feed consisted of 14 % CO₂ (balance N₂) with a flow rate of 61 sccm. The pressure and temperature during the adsorption step were fixed at 130 kPa and 50 °C, and the minimum pressure of the vacuum line was set to 0.5 kPa to ensure dynamic vacuum during the evacuation step. All the VSA steps were carried out co-current with the feed.

The simplest VSA cycle that can be carried out consists of three steps: pressurization, adsorption and evacuation. In the 3-step VSA carried out experimentally, pressurization was carried out with the product end of the adsorber closed, using the feed. The joint duration of the pressurization and adsorption steps was set to 6.1 min, near the breakthrough time of CO₂ in the aforementioned conditions (see Figure 9). To simulate an operation with two columns and constant feed consumption, the time of the evacuation step was set equal to the sum of adsorption and repressurisation steps (see cycle schedule in Figure 14a).

Figure 14. (a) Cycle schedule for the 2 bed 3-step VSA cycle carried out at 50 °C in the one column adsorption unit (F= pressurization with Feed and adsorption at 130 kPa; V=Evacuation); (b) Molar flow rates of CO₂ and N₂ entering and leaving the adsorber and pressure at the adsorber outlet during the cyclic steady state.

Figure 14b represents the molar flow rates of N₂ and CO₂ entering (blue and red lines, respectively) and leaving (blue diamonds and red circles, respectively) the adsorber and the pressure of the bed (orange line) during the simple 3-step VSA cycle carried out. The results shown correspond to cycles 7-28, when the cyclic steady state is established (the molar flow rates at any time in the cycle remain the same in all subsequent cycles). During the pressurization step, the adsorber outlet is closed, and neither N₂ nor CO₂ leave the adsorber. However, when the adsorber outlet is opened, part of the CO₂ fed leaves the column in the raffinate. The loss of CO₂ could be reduced by carrying out a countercurrent repressurisation with raffinate product, to push the CO₂ front back to the feed end. During the adsorption step, a partially decarbonised raffinate is produced. It can be observed that the CO₂ flow rate starts to increase near the end of the adsorption step, which means that the adsorbent is nearly saturated. At the beginning of the evacuation step, the bed pressure is reduced from 130 to 20 kPa in only 20 s. During this rapid depressurization, the molar flow rates of CO₂ and N₂ leaving the adsorber reach their maximum values, decreasing afterwards.

The CO₂ purity of the gas obtained during the evacuation step, calculated by Equation 7 using the data of cycles 7-28 for the integration, is 34 %, with a recovery of 46 % (Equation 8) and a

productivity of $1.5 \text{ mol kg}^{-1} \text{ h}^{-1}$ (Equation 9). The low purity of CO_2 is due to the great amount of N_2 present in the gas phase at the end of the adsorption step, which contaminates the product obtained during the subsequent co-current evacuation. To increase the purity of CO_2 , it is possible to carry out a co-current depressurization to an intermediate pressure to release the N_2 present in the gas phase [64, 65]. For the current VSA cycle configuration, starting the production stage at a pressure of 20 kPa would increase the CO_2 purity up to 48 %, at the expense of a reduction in the recovery down to 38 %. However, these figures are still excessively low. The production stage at low pressure should be carried out countercurrent from the feed end as this part of the bed presents the highest concentration of CO_2 .

In a multibed operation, the product of the initial depressurization, which contains a significant amount of CO_2 , could be used to co-current pressurize another bed through a pressure equalization step, connecting the outlet of a bed at the end of the feed step to the inlet of a bed that needs to be repressurized (Figure 15). The pressure equalization step would increase the purity and recovery of CO_2 and conserve energy [12, 64]. As the gas arising from the initial depressurization is partially depleted in CO_2 , separative work would be also conserved [64].

Figure 15. Cycle schedule for a VSA cycle containing the following steps: E=pressure equalization, F= pressurization with Feed and adsorption at 130 kPa and V=Evacuation.

When the desired product is the component that is preferentially adsorbed, it is common practice to recycle part of the product to carry out a rinse step between the adsorption and evacuation steps to improve its purity. Most of the VSA cycles proposed in the literature for the recovery of CO₂ from flue gases include such step [4, 6-8, 10, 11, 13, 27]. To explore this possibility, a 4-step VSA cycle was carried out consisting on: pressurization with feed, adsorption, rinse and evacuation. In the experimental unit, it is not possible to carry out the recirculation of the product, so the rinse step was carried out with pure CO₂. The duration of the feed and evacuation steps were kept equal to those of the previous cycle for comparison purposes, and the rinse step duration was set equal to that of the feed to simulate an operation with three columns and constant feed consumption (see cycle schedule in Figure 16a). The flow rate of CO₂ during the rinse step in the current cycle was set to give a molar rinse-to-feed (R/F) ratio of 0.7 ($R/F = \text{mol of CO}_2 \text{ fed during the rinse step} / \text{mol of CO}_2 \text{ fed during pressurization and adsorption steps}$).

Figure 16 represents the bed pressure and the N₂ and CO₂ molar flow rates entering and leaving the adsorber during the rinse (Figure 16b) and evacuation steps (Figure 16c), at CSS (symbols correspond to the outlet flow rates during cycles 5-23). The pressurization and adsorption steps are not shown because they were similar to those of the previous 3-step VSA (Figure 14b).

As can be seen from Figure 16b, practically all the CO₂ fed during the rinse step is retained by the adsorbent due to the increase in the partial pressure of CO₂, which increases the driving force for adsorption. The molar flow rate of N₂ in the effluent decreases during the first half of the rinse step, and then approaches a nearly constant pattern. The pressure at the bed outlet, which is related to the outlet flow rate, decreases from 130 kPa to 120 kPa during the rinse step.

As in the 3-step cycle, at the beginning of the evacuation step, the outlet flow rates of N₂ and CO₂ become maxima due to the fast depressurization from 120 to 20 kPa, which takes place in only 20 s. However, in this cycle configuration a new phenomenon is observed: the molar flow rate of CO₂ decreases rapidly after passing through the maximum like that of N₂ but, contrary to the latter, it goes through a second maximum (Figure 16c). The first peak, observed for both CO₂ and N₂, is

attributed to the evacuation of the gas present in the gas phase by the end of the rinse step, while the second peak, only present for CO₂, arises from the desorption of CO₂. The outlet molar flow rate of CO₂ during the evacuation of the 3-step cycle showed a *plateau* at low pressure, rather than a second peak, due to the lower amount of CO₂ adsorbed by the lack of rinse step. This difference can also be observed from the pressure profile: when the evacuation was carried out directly after the adsorption step, the bed reached 10 kPa in only 40 s (Figure 14b), while it took 85 s when the evacuation was carried out after the rinse step. The pressure of the bed by the end of the evacuation step was also lower in the 3-step cycle.

Figure 16. (a) Cycle schedule for the 3-bed 4-step VSA cycle carried out experimentally at 50 °C in the one column adsorption unit (F= Pressurization with Feed and adsorption at 130 kPa; R=Rinse with CO₂; V=Evacuation); bed pressure and molar flow rates of CO₂ and N₂ entering and leaving the adsorber during the Rinse step (b) and Evacuation step (c) at CSS.

The purity of CO₂ obtained during the whole evacuation step of the 4-step cycle, calculated by using the data of cycles 5-23 for the integration, is 61 %, with a recovery of 59 % (Equation 8) and a productivity of 2.1 mol kg⁻¹ h⁻¹ (Equation 9). These values represent a significant improvement to those of the homologous 3-step cycle without rinse. If the recovery and productivity of CO₂ were calculated using Equations 10 and 11, the values would be lower: 32 % and 0.7 mol kg⁻¹ h⁻¹. However,

in the experimental one-column unit, where product recycle is not possible, the definitions of recovery and productivity given by Equations 10 and 11 do not make physical sense, as the CO₂ fed during the rinse step is a net input into the material balance of the cycle. Nevertheless these values have been included in Table 5 for comparison purposes.

Table 5. Summary of VSA results for the different configurations evaluated

VSA steps	CO ₂ purity ^a (%)	CO ₂ recovery (%)	Productivity (%)
PF-F-V	34	46 ^b	1.5 ^d
PF-F-VI-VII	48	38 ^b	1.3 ^d
PF-F-R-V	61	59 ^b / 32 ^c	2.1 ^d / 0.7 ^e
PF-F-R-VI+VII	76	52 ^b / 20 ^c	1.9 ^d / 0.4 ^e
PF-F-R-V	62	73 ^b / 59 ^c	2.6 ^d / 1.2 ^e
PF-F-R-VI+VII	79	59 ^b / 34 ^c	2.1 ^d / 0.7 ^e
PF-F-R-V-L	67	79 ^b / 70 ^c	2.9 ^d / 1.5 ^e
PF-F-R-VI-VII-L	74	67 ^b / 48 ^c	2.4 ^d / 1.0 ^e
PF-F-R-VT-L	67	88 ^b / 81 ^c	3.1 ^d / 1.7 ^e
PF-F-R-VI-VTII-L	75	84 ^b / 73 ^c	2.9 ^d / 1.5 ^e

PF=Pressurization with Feed; F=Feed; V=Evacuation step; VI=co-current depressurization down to 20 kPa; VII=Evacuation at P≤20 kPa; R= Rinse with pure CO₂; L=Light purge with pure N₂ at low pressure; VT= Evacuation coupled with moderate temperature rise; ^a Calculated at CSS using Equation 7; ^b calculated at CSS using Equation 8; ^c calculated at CSS using Equation 10; ^d Calculated at CSS using Equation 9; ^e Calculated at CSS using Equation 11.

On the other hand, if the production stage starts at a pressure of 20 kPa, the purity of CO₂ increases up to 76 % with a recovery of 52 % (Equation 8) and a productivity of 1.9 mol kg⁻¹ h⁻¹ (Equation 9). As mentioned above, in a real multibed operation, the product of the initial depressurization would be used to co-current pressurize another bed through a pressure equalization step, increasing the recovery of CO₂ and conserving energy. The effluent gas during the rinse step is produced at a pressure close to that of the feed and presents globally a feed-like composition, which would facilitate its recycling to improve the purity and recovery of CO₂ [8].

To improve the recovery of CO₂, the evacuation step of the 4-step cycle was extended (note that CO₂ was still being desorbed by the end of the evacuation step in Figure 16c). The duration of the feed step was kept equal to that of the previous cycles, and the duration of the rinse step was shortened to account for the extension of the evacuation step (see cycle schedule in Figure 17a). The rinse-to-feed ratio was kept constant at 0.7 by increasing the molar flow rate of CO₂ during the rinse step.

As can be seen from Figure 17b, the outlet molar flow rate of N₂ follows now a monotonic decreasing trend during the whole rinse step. Apparently, the shorter rinse step carried out with a

higher molar flow rate of CO₂ displaces the N₂ present in the gas phase more effectively (the residence time of CO₂ is lower, so it has less time to adsorb). Differences can also be observed in the pressure profiles during the rinse and evacuation steps. During the rinse step, the pressure of the bed takes longer time to reach 120 kPa, which now occurs near the end of the rinse step. The initial depressurization of the evacuation step was similar to the previous cycles; however, comparing the 4-step cycles with different rinse and evacuation times, the final depressurization to 10 kPa was faster in this latter case (65 s).

(a)

(b)

(c)

Figure 17. (a) Cycle schedule for the 3-bed 4-step VSA cycle carried out experimentally in the one column adsorption unit (F= Pressurization with Feed and adsorption at 130 kPa; R=Rinse with CO₂; V=Evacuation); bed pressure and molar flow rates of N₂ and CO₂ entering and leaving the adsorber during the rinse (b) and evacuation (c) steps at CSS.

The longer evacuation time increased significantly the recovery of CO₂ obtained during the whole evacuation step up to 73 % (Equation 8), and the productivity up to 2.6 mol kg⁻¹ h⁻¹ (Equation 9), with a CO₂ purity of 62 %, which is slightly above that of the previous configuration. By starting the production step at 20 kPa, the CO₂ purity can be increased to 79 % at a lower recovery of 59 %. As discussed before, the product of the initial co-current depressurization should be used to pressurize a regenerated bed in a pressure equalization step to save energy and improve recovery.

To improve further the recovery of CO₂ it is also possible to carry out a purge step at low pressure after the evacuation step by recycling part of the raffinate product or by using an external purge [7, 11, 12, 64]. To explore this 5-step cycle configuration in the experimental unit, a small flow rate of pure N₂ was used. The feed and rinse step times and flow rates were kept equal to those used in the previous cycle configuration, but the last stage of the evacuation step was substituted by the purge step at low pressure (see cycle schedule in Figure 18a).

Figure 18. (a) Cycle schedule of the 3-bed 5-step VSA cycle carried out experimentally in the one column adsorption unit (F= Pressurization with feed and adsorption at 130 kPa; R=Rinse with CO₂; V=Evacuation; L= Light purge with N₂); bed pressure and molar flow rates of N₂ and CO₂ entering and leaving the adsorber during the evacuation (b) and purge (c) steps at CSS.

The behaviour of the outlet molar flow rates of CO₂ and N₂ during the evacuation step at CSS (Figure 18b) is similar to that observed in the previous cycles with rinse step: two maxima are observed in the outlet molar flow rate of CO₂, while that of N₂ presents a single maximum during the initial stage of the co-current depressurization. However, depressurization is faster than in the previous cycles: the bed reaches 10 kPa in only 35 s. Moreover, the final pressure by the end of the evacuation step is lower than in the homologous 4-step cycle. During the light purge step (Figure 18 c) part of the CO₂ that was still present in the bed by the end of the evacuation step is displaced by the incoming N₂. The molar flow rate of N₂ leaving the adsorber follows an upward trend during the purge step: it is minimal at the beginning and tends to meet the inlet flow rate by the end of the step. By extending the length of the purge, the CO₂ recovery could be increased (there is still CO₂ leaving the adsorber by the end of the purge step, but at the expense of a lower purity; the product becomes increasingly contaminated by N₂). A trade-off between purity, recovery and power should be considered when conducting light purge [12]. The CO₂ purity of the product gas during the purge step calculated using Equation 7 and integrating the data from cycles 5-19 is 84 %, which is above that of the product of the co-current evacuation step (64 %). If all the gas leaving the adsorber during the evacuation and purge steps was to be collected as product, its CO₂ purity would be 67 % CO₂ with a recovery of 79 % (Equation 8) and a productivity of 2.9 mol kg⁻¹ h⁻¹ (Equation 9). These figures are better than those obtained by the 4-step configuration without light rinse (see Table 5). By starting the production step at a pressure of 20 kPa, the purity of the product can be increased to 74 %. As discussed for the previous cycle configurations, the product of the initial depressurization should be exploited to carry out a pressure equalization step, to conserve energy and improve CO₂ recovery.

The effect of rinse flow rate was evaluated using the latter VSA configuration, keeping constant all the cycle parameters except the flow rate of CO₂ fed during the rinse step. Figure 19 shows the effect of varying the rinse-to-feed ratio (R/F) in the recovery and purity of CO₂. Both recovery and

purity go through a maximum at $R/F = 0.7$. Increasing further the rinse flow rate causes a decrease in recovery (more pronounced if defined by Equation 10), with no extra gain in purity.

Figure 19. Effect of rinse flow rate on CO₂ purity and recovery.

Finally, a VTSA cycle was carried out. The cycle schedule was similar to that of Figure 18a, although in this case the adsorber was heated up to 70 °C during the evacuation step and cooled down to the adsorption temperature (50 °C) during the purge step (see Figure 20). This moderate temperature swing shifts the CO₂ recovery to 88 % and the productivity to 3.1 mol kg⁻¹ h⁻¹ while maintaining the CO₂ purity at 67 % if all the gas that leaves the adsorber during the evacuation and purge steps was to be collected as product. As in the previous cases, CO₂ purity can be improved by starting the production step at subatmospheric pressure. For example, by starting the production step at a pressure of 20 kPa, the CO₂ purity shifted to 75 % with a recovery of 84 % (Equation 8) and a productivity of 2.9 mol kg⁻¹ h⁻¹ (Equation 9). As mentioned before, in a multi-bed process the outlet gas from the initial depressurization would be used to co-current pressurize another vessel in a pressure equalization step, with the subsequent energy saving and increase in recovery.

Figure 20. Molar flow rates of N_2 and CO_2 entering and leaving the adsorber and bed temperature and pressure during the cyclic steady state of the VTSA cycle carried out in the experimental unit.

Although the purity of CO_2 of the cycle configurations evaluated experimentally (see summary in Table 5) is still not sufficient to meet transport and storage specifications, the values obtained for CO_2 recovery and productivity are relatively large compared to values found in the literature using different materials and cycle configurations. A two-stage PSA process could be used to meet the required CO_2 purity [17, 28]. Moreover, the minimum pressure achieved during the here presented cycles (5-10 kPa) is relatively large, and has been proposed as the optimal value to minimize the cost of postcombustion CO_2 capture [9]. A deeper vacuum level would improve the CO_2 purity and recovery, but at the expense of higher power consumption and larger capital cost [9, 10]. The VSA cycles presented in this work do not pretend to be optimal cycles, but to illustrate the versatility of the coffee-based adsorbent to separate CO_2 in postcombustion conditions. The produced data will be used to validate an adsorption model that will be used to design the optimised adsorption-desorption cycles.

Conclusions

An environmentally friendly and low-cost adsorbent, PPC, has been produced from an abundant residue of the food industry, coffee grounds, by single-step activation with CO_2 . This adsorbent

presents an adequate size for its use in fixed-bed adsorption operation: it consists on regular pellets with a diameter of 2.7 mm and an average height of 1.9 mm. The bulk density of this material is relatively high, especially for biomass-based carbons, which is highly desirable as it would reduce the volume of the final adsorber. PPC is a microporous adsorbent with a narrow pore size distribution, suitable for the adsorption of CO₂ at low partial pressures, which is the case of postcombustion CO₂ capture (patent application filed [1]).

The CO₂ adsorption capacity of the coffee based carbon at low pressure is above that of commercial activated carbons taken as reference: values between 0.8 and 1.2 mmol g⁻¹ at 15 kPa in the temperature range between 25 and 50 °C which represent plausible operation conditions for a postcombustion capture unit. A temperature dependant Toth adsorption model showed adequate to describe the equilibrium of adsorption of pure CO₂ and N₂ in the temperature and pressure range evaluated.

Single pellet adsorption experiments showed that the here presented adsorbent presents small intraparticle mass transfer resistance. Breakthrough experiments showed steep breakthrough curves, which confirmed that the overall mass transfer resistance for this adsorbent is small, which is highly desirable for a rapid swing adsorption process.

The breakthrough experiments demonstrated that CO₂ can be separated from CO₂/N₂ streams in conditions representative of postcombustion conditions (9-31 % CO₂, 50 °C, 130 kPa) with CO₂/N₂ equilibrium separation factor values between 15 and 25. IAST prediction underestimates the amount of N₂ coadsorption thus overestimating the CO₂/N₂ equilibrium separation factor.

Different VSA cycle configurations were evaluated under postcombustion capture conditions to illustrate the adsorbent performance in cyclic operation. CO₂ was concentrated from 14 % up to 75 % with a recovery of 84 % and a productivity of 2.9 mol kg⁻¹ h⁻¹ under a VTSA cycle configuration consisting of pressurization with feed, adsorption at 50 °C and 130 kPa, rinse with CO₂, co-current depressurization down to 20 kPa, and a production stage consisting of evacuation down to 10 kPa with simultaneous heating up to 70 °C and a light purge step at 10 kPa. Although the purity of CO₂ of

the cycles evaluated experimentally is not sufficiently high to meet transport and storage specifications, CO₂ recovery and productivity are large considering that the minimum pressure reached within the cycle is relatively high (10 kPa), which would significantly reduce the operating and capital cost of the adsorption capture unit. No signs of adsorbent deactivation were observed during the course of this investigation.

Acknowledgments

Work carried out with financial support from the Spanish MINECO (Project ENE2011-23467), co-financed by the European Regional Development Fund (ERDF). M.G.P. acknowledges funding from the CSIC (JAE-Doc program), and A.S.G. acknowledges a contract from the MINECO (FPI program); both programs are co-financed by the European Social Fund.

References

- [1] González AS, Plaza MG, Pevida C, Rubiera F. *Procedimiento de obtención de un adsorbente que utiliza residuos de café postconsumo y su utilización para la adsorción de CO₂*. CSIC. Application number: P201331003. Spain, 2013.
- [2] EC. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the future of Carbon Capture and Storage in Europe. Brussels: European Commission; 2013.
- [3] IPCC. IPCC special report on carbon dioxide capture and storage. Cambridge, United Kingdom and New York, NY, USA: IPCC; 2005.
- [4] Chue KT, Kim JN, Yoo YJ, Cho SH, Yang RT. Comparison of activated carbon and zeolite 13X for CO₂ recovery from flue gas by pressure swing adsorption. *Ind. Eng. Chem. Res.* 1995;34:591-8.
- [5] Na B-K, Koo K-K, Eum H-M, Lee H, Song H. CO₂ recovery from flue gas by PSA process using activated carbon. *J. Chem. Eng. Data* 2001;18:220-7.
- [6] Takamura Y, Narita S, Aoki J, Hironaka S, Uchida S. Evaluation of dual-bed pressure swing adsorption for CO₂ recovery from boiler exhaust gas. *Sep. Purif. Technol.* 2001;24:519-28.
- [7] Park JH, Beum HT, Kim JN, Cho SH. Numerical analysis on the power consumption of the PSA process for recovering CO₂ from flue gas. *Ind. Eng. Chem. Res.* 2002;41:4122-31.
- [8] Na B-K, Lee H, Koo K-K, Song HK. Effect of rinse and recycle methods on the pressure swing adsorption process to recover CO₂ from power plant flue gas using activated carbon. *Ind. Eng. Chem. Res.* 2002;41:5498-503.

- [9] Ho MT, Allinson GW, Wiley DE. Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption. *Ind. Eng. Chem. Res.* 2008;47:4883-90.
- [10] Zhang J, Webley PA, Xiao P. Effect of process parameters on power requirements of vacuum swing adsorption technology for CO₂ capture from flue gas. *Energ. Convers. Manage.* 2008;49:346-56.
- [11] Reynolds S, Mehrotra A, Ebner A, Ritter J. Heavy reflux PSA cycles for CO₂ recovery from flue gas: Part I. Performance evaluation. *Adsorption* 2008;14:399-413.
- [12] Zhang J, Webley PA. Cycle development and design for CO₂ capture from flue gas by vacuum swing adsorption. *Environ. Sci. Technol.* 2008;42:563-9.
- [13] Liu Z, Wang L, Kong X, Li P, Yu J, Rodrigues AE. Onsite CO₂ capture from flue gas by an adsorption process in a coal-fired power plant. *Ind. Eng. Chem. Res.* 2012;51:7355-63.
- [14] Merel J, Clausse M, Meunier F. Experimental investigation on CO₂ post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites. *Ind. Eng. Chem. Res.* 2008;47:209-15.
- [15] Grande CA, Ribeiro RPPL, Rodrigues AE. CO₂ capture from NGCC power stations using electric swing adsorption (ESA). *Energy & Fuels* 2009;23:2797–803.
- [16] Radosz M, Hu X, Krutkramelis K, Shen Y. Flue-gas carbon capture on carbonaceous sorbents: toward a low-cost multifunctional carbon filter for "green" energy producers. *Ind. Eng. Chem. Res.* 2008;47:3783-94.
- [17] Ishibashi M, Ota H, Akutsu N, Umeda S, Tajika M, Izumi J, Yasutake A, Kabata T, Kageyama Y. Technology for removing carbon dioxide from power plant flue gas by the physical adsorption method. *Energ. Convers. Manage.* 1996;37:929-33.
- [18] Plaza MG, García S, Rubiera F, Pis JJ, Pevida C. Post-combustion CO₂ capture with a commercial activated carbon: Comparison of different regeneration strategies. *Chem. Eng. J.* 2010;163:41-7.
- [19] Plaza MG, García S, Rubiera F, Pis JJ, Pevida C. Evaluation of ammonia modified and conventionally activated biomass based carbons as CO₂ adsorbents in postcombustion conditions. *Sep. Purif. Technol.* 2011;80:96-104.
- [20] Wang L, Liu Z, Li P, Yu J, Rodrigues AE. Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. *Chem. Eng. J.* 2012;197:151-61.
- [21] Dutcher B, Adidharma H, Radosz M. Carbon filter process for flue-gas carbon capture on carbonaceous sorbents: steam-aided vacuum swing adsorption option. *Ind. Eng. Chem. Res.* 2011;50:9696-703.
- [22] Haghpanah R, Nilam R, Rajendran A, Farooq S, Karimi IA. Cycle synthesis and optimization of a VSA process for postcombustion CO₂ capture. *AIChE J.* 2013.
- [23] Agarwal A, Biegler LT, Zitney SE. A superstructure-based optimal synthesis of PSA cycles for post-combustion CO₂ capture. *AIChE J.* 2010;56:1813-28.
- [24] Yu CH, Huang CH, Tan CS. A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol and Air Quality Research* 2012;12:745-69.

- [25] Martín CF, Plaza MG, Pis JJ, Rubiera F, Pevida C, Centeno TA. On the limits of CO₂ capture capacity of carbons. *Sep. Purif. Technol.* 2010;74:225-9.
- [26] Presser V, McDonough J, Yeon S-H, Gogotsi Y. Effect of pore size on carbon dioxide sorption by carbide derived carbon. *Energ. Environ. Sci.* 2011;4:3059-66.
- [27] Kikkinides ES, Yang RT, Cho SH. Concentration and recovery of carbon dioxide from flue gas by pressure swing adsorption. *Ind. Eng. Chem. Res.* 1993;32:2714-20.
- [28] Shen C, Liu Z, Li P, Yu J. Two-Stage VPSA Process for CO₂ Capture from Flue Gas Using Activated Carbon Beads. *Ind. Eng. Chem. Res.* 2012;51:5011-21.
- [29] Delgado JA, Uguina MA, Sotelo JL, Águeda VI, Sanz A, Gómez P. Numerical analysis of CO₂ concentration and recovery from flue gas by a novel vacuum swing adsorption cycle. *Computers & Chemical Engineering* 2011;35:1010-9.
- [30] Xu D, Xiao P, Zhang J, Li G, Xiao G, Webley PA, Zhai Y. Effects of water vapour on CO₂ capture with vacuum swing adsorption using activated carbon. *Chem. Eng. J.* 2013;230:64-72.
- [31] Xu D, Zhang J, Li G, Xiao P, Webley P, Zhai Y-c. Effect of water vapor from power station flue gas on CO₂ capture by vacuum swing adsorption with activated carbon. *Journal of Fuel Chemistry and Technology* 2011;39:169-74.
- [32] Plaza MG, Pevida C, Arias B, Casal MD, Martín CF, Fermoso J, Rubiera F, Pis JJ. Different approaches for the development of low-cost CO₂ adsorbents. *J. Environ. Eng.-ASCE* 2009;135:426-32.
- [33] Plaza MG, Pevida C, Arias B, Fermoso J, Casal MD, Martín CF, Rubiera F, Pis JJ. Development of low-cost biomass-based adsorbents for postcombustion CO₂ capture. *Fuel* 2009;88:2442-7.
- [34] Plaza MG, Pevida C, Arias B, Fermoso J, Rubiera F, Pis JJ. A comparison of two methods for producing CO₂ capture adsorbents. *Energ. Procedia* 2009;1:1107-13.
- [35] Plaza MG, Pevida C, Martín CF, Fermoso J, Pis JJ, Rubiera F. Developing almond shell-derived activated carbons as CO₂ adsorbents. *Sep. Purif. Technol.* 2010;71:102-6.
- [36] Plaza MG, Rubiera F, Pis JJ, Pevida C. Ammoxidation of carbon materials for CO₂ capture. *Appl. Surf. Sci.* 2010;256:6843-9.
- [37] Plaza MG, Pevida C, Pis JJ, Rubiera F. Evaluation of the cyclic capacity of low-cost carbon adsorbents for post-combustion CO₂ capture. *Energ. Procedia* 2011;4:1228-34.
- [38] Plaza MG, González AS, Pevida C, Pis JJ, Rubiera F. Valorisation of spent coffee grounds as CO₂ adsorbents for postcombustion capture applications. *Appl. Energ.* 2012;99:272-9.
- [39] Plaza MG, González AS, Pis JJ, Rubiera F, Pevida C. Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO₂ capture. *Appl. Energ.* 2014;114:551-62.
- [40] ICO. Monthly Coffee Market Report September 2012: International Coffee Organization; 2013.
- [41] Murthy PS, Madhava Naidu M. Sustainable management of coffee industry by-products and value addition—A review. *Resour. Conserv. Recy.* 2012;66:45-58.

- [42] Silva MA, Nebra SA, Machado Silva MJ, Sanchez CG. The use of biomass residues in the Brazilian soluble coffee industry. *Biomass Bioenergy* 1998;14:457-67.
- [43] Sprules RK. *Coffee-based solid fuel composition*. Application number: 09/086797. US 5910454; United States, 1999.
- [44] Kondamudi N, Mohapatra SK, Misra M. Spent coffee grounds as a versatile source of green energy. *J. Agric. Food Chem.* 2008;56:11757-60.
- [45] Franca AS, Nunes AA, Oliveira LS. Activated carbons based on solid residues from coffee biodiesel production. *J. Biotechnol.* 2008;136:S654-S5.
- [46] Boonamnuayvitaya V, Sae-ung S, Tanthapanichakoon W. Preparation of activated carbons from coffee residue for the adsorption of formaldehyde. *Sep. Purif. Technol.* 2005;42:159-68.
- [47] Kante K, Nieto-Delgado C, Rangel-Mendez JR, Bandosz TJ. Spent coffee-based activated carbon: Specific surface features and their importance for H₂S separation process. *J. Hazard. Mater.* 2012;201–202:141-7.
- [48] Reffas A, Bernardet V, David B, Reinert L, Lehocine MB, Dubois M, Batisse N, Duclaux L. Carbons prepared from coffee grounds by H₃PO₄ activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL. *J. Hazard. Mater.* 2010;175:779-88.
- [49] Namane A, Mekarzia A, Benrachedi K, Belhaneche-Bensemra N, Hellal A. Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl₂ and H₃PO₄. *J. Hazard. Mater.* 2005;119:189-94.
- [50] Evans MJB, Halliop E, MacDonald JAF. The production of chemically-activated carbon. *Carbon* 1999;37:269-74.
- [51] Inomata K, Kanazawa K, Urabe Y, Hosono H, Araki T. Natural gas storage in activated carbon pellets without a binder. *Carbon* 2002;40:87-93.
- [52] Hirata M, Kawasaki N, Nakamura T, Matsumoto K, Kabayama M, Tamura T, Tanada S. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. *J. Colloid Interface Sci.* 2002;254:17-22.
- [53] González AS, Plaza MG, Pis JJ, Rubiera F, Pevida C. Post-combustion CO₂ capture adsorbents from spent coffee grounds. *Energ. Procedia* 2013;37:134-41.
- [54] Dubinin MM. Properties of active carbons. In: Walker J, L. P, editors. *Chemistry and physics of carbon*, New York: Marcel Dekker Inc; 1966, p. 51-120.
- [55] Do DD. *Adsorption analysis: equilibria and kinetics*. Singapore: Imperial College Press; 1998.
- [56] Plaza MG, Thurecht KJ, Pevida C, Rubiera F, Pis JJ, Snape CE, Drage TC. Influence of oxidation upon the CO₂ capture performance of a phenolic-resin-derived carbon. *Fuel Process. Technol.* 2013;110:53-60.
- [57] Li P-Z, Zhao Y. Nitrogen-Rich Porous Adsorbents for CO₂ Capture and Storage. *Chemistry – An Asian Journal* 2013;8:1680-91.

- [58] Liu Y, Wilcox J. Effects of Surface Heterogeneity on the Adsorption of CO₂ in Microporous Carbons. *Environ. Sci. Technol.* 2012;46:1940-7.
- [59] Yin G, Liu Z, Liu Q, Wu W. The role of different properties of activated carbon in CO₂ adsorption. *Chem. Eng. J.* 2013;230:133-40.
- [60] Tsunoda R, Ando J-i. Adsorption of water vapor on active carbons: Estimation of the average pore width from the magnitude of the hysteresis loop. *J. Colloid Interface Sci.* 1991;146:291-3.
- [61] González AS, Plaza MG, Rubiera F, Pevida C. Sustainable biomass-based carbon adsorbents for post-combustion CO₂ capture. *Chem. Eng. J.* 2013;230:456-65.
- [62] Ruthven DM. Principles of adsorption and adsorption processes. New York: John Wiley and Sons; 1984.
- [63] Bird RB, Stewart WE, Lightfoot EN. Transport Phenomena. New York: John Wiley & Sons; 1960.
- [64] Ruthven DM, Farooq S, Knaebel KS. Pressure swing adsorption: John Wiley & Sons, Inc.; 1994.
- [65] Guerin de Montgareuil P, Domine D. *Process for separating a gaseous binary mixture by adsorption*. Application number: 3,155,468; U.S., 1964.