Sustainable biomass-based carbon adsorbents for post-combustion CO₂ capture

A.S. González, M.G. Plaza, F. Rubiera¹, C. Pevida

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

Abstract

Sustainable carbon adsorbents have been produced from biomass residues by single-step activation with CO₂. The activation conditions were optimised to develop narrow micropores in order to maximise the CO₂ adsorption capacity of the carbons under post-combustion conditions. The equilibrium of adsorption of pure CO₂ and N₂ was measured between 0 and 50 °C up to 120 kPa for the outstanding carbons. The CO₂ adsorption capacity measured at low pressures is among the highest ever reported for carbon materials (0.6-1.1 mmol g⁻¹ at 15 kPa and 25-50 °C), and the average isosteric heat of adsorption is typical of a physisorption process: 27 kJ mol⁻¹. Dynamic experiments carried out in a fixed-bed adsorption unit showed fast adsorption and desorption kinetics and a high CO₂-over-N₂ selectivity. These adsorbents are able to separate a mixture with 14 % CO₂ (balance N₂) at 50 °C, conditions that can be considered as representative of post-combustion conditions, and they can be easily regenerated.

Keywords: CO₂ capture, adsorption, biomass, carbon materials

1. Introduction

There is an urgent need to stabilise the greenhouse gas levels in the atmosphere before permanent damage is done to the climatic system [1]. Given the current energy scenario, the implementation of Carbon Capture for Use and Storage (CCUS) technologies at large scale is mandatory for achieving the required reduction of greenhouse gas emissions in time [2]. Post-combustion CO₂ capture, in which CO₂ is separated after the combustion of fossil fuels in large stationary sources, can be exploited to retrofit existing facilities and newly designed plants, contributing to the overall mitigation effort in the mid-term. The main challenges of this technology are the high flow rate of flue gases and the low partial pressure of CO₂, which reduces the separation potential. Although no post-combustion capture units have been installed yet at full scale, large demonstration projects are under way based on amine scrubbing. This technology is energy intensive due to the high steam consumption required to

¹ *corresponding author*. Tel. +34 985 11 90 90; Fax: +34 985 29 76 62
e-mail address: frubiera@incar.csic.es

regenerate the diluted amine solvent: a parasitic loss of 30% of the net power is expected from the use of MEA processes [3]. Adsorption is a separation technology with the potential to reduce the energy penalty of the capture step compared to amine scrubbing [4-8]. The main advantages of adsorption processes over amine scrubbing are the lower energy requirements and the higher capacity on a volume basis [9]. Although on a lower scale than the benchmark amine scrubbing, demonstration projects based on solid sorbents are also being developed to put this technology to the test [10]. A recent pilot scale study of CO₂ capture carried out with flue gases from an actual coal-fired power plant, has demonstrated that energy consumption of a VPSA process can be lower than that of the amine scrubbing based case [11].

The ideal post-combustion adsorbent needs to offer a series of characteristics: availability, CO₂ selectivity, sufficient adsorption capacity, a high stability (long life), ease of regeneration, and low cost. Carbon adsorbents fulfil all these requirements: they can be obtained at low cost from a renewable and globally available source (biomass), they are selective towards CO₂, they can be easily regenerated, and unlike other physical adsorbents such as zeolites or MOFs, they are hydrophobic and show high stability in humid conditions.

As mentioned above, good quality and sustainable activated carbons and carbon molecular sieves can be obtained from biomass precursors [12, 13]. The production of carbon adsorbents from biomass precursors involves either physical or chemical activation [14]. In chemical activation the precursor is carbonised in the presence of a chemical agent (KOH, NaOH, H₃PO₄, K₂CO₃, ZnCl, *etc.*). Industrially, it is common to obtain activated carbons from wood by the phosphoric acid process; activation with KOH is also frequent. The main disadvantage of chemical activation is the thorough washing necessary to eliminate the excess of activating agent from the activated product. The chemical agent can represent up to 1000 % of the precursor weight [15], and thus needs to be recycled to the process. Physical activation has a lower environmental impact, as it uses CO₂, H₂O or air as the activating agent. Although this process is generally carried out in a two-step procedure, in which the precursor is first carbonised in an inert atmosphere and then activated, it can also be carried out in a single step process [16-19]. The avoidance of a separate carbonisation step can reduce the operation and installation costs. Moreover, single-step activation of agricultural byproducts can lead to activated carbons with better characteristics, in terms of surface area and porosity development compared to those obtained by the two-step procedure [16, 18]. Due to aforementioned advantages, single step activation with CO₂ was selected to prepare low-cost and sustainable carbon adsorbents from renewable biomass products: almond shells and olive

stones. In previous studies, these precursors have been shown to be adequate to obtain microporous carbons with good properties for use as CO₂ adsorbents [20-22].

By changing the activation conditions during carbon production, the pore size distribution can be tailored to a particular application. For post-combustion capture, it is important to maximise the volume of micropores below 0.5-0.8 nm, as these are responsible for the adsorption of CO₂ at low partial pressures [23, 24]. In this work, optimised carbons obtained by the single-step procedure were evaluated as CO₂ adsorbents under post-combustion conditions.

2. Materials and Methods

Olive stones and almond shells were crushed and sieved, and samples with a particle size of between 1 and 3 mm were selected for further treatment. The elemental analysis and characterisation of the raw materials can be found elsewhere [20]. Single-step activation with CO₂ was carried out using a double-jacket quartz reactor in a vertical furnace. The effect of the holding time was assessed by preparing series of samples in a small reactor (I.D. 2 cm) loaded with nearly 3 g of raw biomass and using a flow rate of CO₂ of 100 sccm. The heating rate was 10 °C min⁻¹ in all cases. The overall yield of the process (g of carbon adsorbent obtained per 100 g of raw biomass) can be found in Tables 1 and 2.

The carbons obtained were characterised by physical adsorption of N₂ at -196 °C using a volumetric apparatus. The samples were evacuated overnight at 100 °C prior to the adsorption measurements. The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The Dubinin-Radushkevich (DR) equation [25] was used to estimate the total micropore volume from the adsorption isotherm of N₂ at -196 °C (V_{DR-N_2}). The average micropore width (L) was calculated by means of the Stoeckli-Ballerini equation [26]. Apparent BET surface areas [27] are given for reference purposes.

The CO₂ adsorption capacity of all the prepared carbons was preliminarily evaluated in a thermogravimetric analyser at atmospheric pressure. Prior to the adsorption measurements, the samples were dried in situ in an Ar flow at 100 °C for 1 h, and then allowed to cool down to 25 °C. The CO₂ uptake was then evaluated from the mass gained by the sample when the feed gas was switched to a pure flow of CO₂. Once the equilibrium was attained at 25 °C, the temperature was increased at 0.5 °C min⁻¹ up to 100 °C to evaluate the adsorption capacity in this temperature range. The final temperature of 100 °C was held for 1 h to ensure that equilibrium had been attained at this temperature. Finally, the samples were regenerated by

switching the feed gas back to argon. The amount of CO₂ adsorbed is expressed as mmol per g of adsorbent. The mass of dry sample by the end of the drying step has been taken as the reference mass for the whole experiment (Ar adsorption at 100 °C is considered negligible). Buoyancy effects were corrected by running a blank experiment.

Once the most promising adsorbents had been identified, carbon production was scaled up using a larger reactor (I.D. 3.9 cm) keeping the superficial velocity constant. Two carbons were produced at the larger scale, one from each raw material: olive stones (OS) and almond shells (AS).

Gas separation processes can be driven by equilibrium or kinetic selectivity towards one adsorbate present in a gas mixture. Therefore it is of the utmost importance to study the equilibrium and dynamics of adsorption of an adsorbent for a particular application. The potential of the selected carbons, AS and OS, as adsorbents for post-combustion capture applications, was further evaluated by equilibrium and dynamic adsorption experiments.

To gain an insight into the equilibrium of adsorption of the major flue gas components under the conditions of interest for the post-combustion case, the adsorption isotherms of pure CO₂ and N₂ were obtained at 0, 25 and 50 °C between 0 and 120 kPa. Measurement of the adsorption isotherms at different temperatures entailed assessing the isosteric heat of adsorption by means of the Clausius-Clapeyron equation:

$$(-\Delta H) = -R_g \left[\frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right]_{C_{\mu}} \quad (1)$$

where $(-\Delta H)$ is the isosteric heat of adsorption at a selected adsorbed amount C_{μ} , T is the temperature, P is the pressure of the gas phase and R_g the universal constant of gases.

Equilibrium data were fitted to the Sips adsorption model:

$$C_{\mu} = C_{\mu s} \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \quad (2)$$

where $C_{\mu s}$ is the saturation capacity, b is the affinity constant, P is the pressure and n is a parameter that characterises the heterogeneity of the system. Parameters $C_{\mu s}$, b , and n were fitted to minimise the sum of square residuals (SQR) between the experimental data and the model prediction:

$$SQR = \sum_T \left[\frac{100}{N} \sum_{i=1}^N (C_{p,exp} - C_{p,calc})_i^2 \right] \quad (3)$$

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

The affinity constant was considered temperature dependent according to Equation 3:

$$b = b_0 \exp \left[\frac{Q}{R_g T_0} \left(\frac{T_0}{T} \right) - 1 \right] \quad (4)$$

where b_0 is the affinity constant at a reference temperature (T_0) (here taken as 0 °C), Q is a measure of the heat of adsorption, and R_g is the universal constant of gases. Parameter n was considered temperature dependent as expressed by the following equation [28]:

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T} \right) \quad (5)$$

Multicomponent dynamic adsorption experiments were carried out in a fixed bed adsorption unit consisting of a stainless steel adsorber of 9.12 mm internal diameter equipped with temperature control. The composition of the effluent was analysed by a gas microchromatograph, and its flow rate was determined by adding a known flow of oxygen before the analysis section. Further details of the experimental device can be found elsewhere [29]. The adsorbents were regenerated before the adsorption experiments by purging the bed with helium at 150 °C for 1 h. Binary CO₂/N₂ breakthrough curves were obtained by feeding a mixture with 14 % CO₂ (balance N₂) to the bed initially full of helium at the desired temperature. The temperature of the solid was kept constant during the experiments, and the pressure at the bed outlet was 120 kPa. Details of the adsorbent beds can be found in Table 6.

Breakthrough experiments were simulated using Aspen Adsorption V7.2. The fixed-bed adsorption model used makes the following assumptions: isothermal condition; negligible radial mixing; pressure drop given by Ergun equation; mass transfer described by a lumped overall resistance which is a linear function of the particle-averaged adsorbed phase concentration (linear driving force approximation); and multicomponent adsorption equilibrium described by the Sips model for pure components making use of the ideal Adsorbed Solution (IAS) Theory to account for competitive adsorption. Further details of the simulation environment and the model can be found elsewhere [30].

3. Results and Discussion

3.1. Sample preparation

3.1.1. CO₂ reactivity of raw materials

Figure 1 shows the residual mass and the rate of mass loss profiles of raw olive stones and almond shells during heating at 15 °C min⁻¹ in CO₂ flow, recorded in a thermogravimetric analyser. Up to 700 °C, the profiles are similar to those obtained in inert atmosphere: the two distinct maxima observed in the derivative curves, at approximately 280 and 350 °C, are attributed to the thermal decomposition of biomass constituents: hemicellulose together with lignin and cellulose, respectively [31]. At 700 °C, the devolatilisation of biomass is nearly complete: the rate of mass loss tends to zero, and the remaining solid (*char*), which constitutes 26-27% of the starting mass, is mainly composed by carbon.

At 750 °C in the case of almond shells, and at 800 °C in the case of olive stones, the rate of mass loss starts to increase again slightly (see the inset in the upper right corner of the figure). This is due to carbon consumption from the endothermic reaction with CO₂, which is responsible for the development of porosity:

The activation temperature plays an important role in porosity development: the temperature must be high enough for the reaction to occur. However, as the temperature increases, the reaction increases faster than the diffusion rate, which is undesirable for micropore formation. For this reason the onset reaction temperatures shown in Figure 1, 750 °C in the case of almond shells, and 800 °C in the case of olive stones, were selected as the temperatures for activation in the fixed bed reactor.

3.1.2. Effect of holding time

Two series of carbons were produced from olive stones and almond shells by single step activation at the previously selected temperatures at a flow rate of 100 sccm of CO₂ in a fixed bed reactor (I.D. 2 cm) for increasing periods of time.

The adsorption isotherms of N₂ at -196 °C of the olive stones and almond shells series are of Type I according to the BDDT classification (see supporting information), and do not show hysteresis loop, which is characteristic of microporous solids. This can also be observed by the

ratio of micropore to total pore volume shown in Tables 1 and 2. However, as activation proceeds, there is a progressive opening of the knee which is associated with the widening of the micropores (see the steady increase in the average micropore width (L_{N2}) in Table 1 and 2). The total pore volume, V_p , and BET surface area, S_{BET} , increase with soaking time, going through a maximum and decreasing above this point for both series (see Tables 1 and 2). This can be explained by the fact that at high activation times, the walls of adjacent micropores collapse, giving rise to wider micropores. The maximum pore volume ($0.51 \text{ cm}^3 \text{ g}^{-1}$) was attained for the olive stones, and for a holding time of 6 h (Table 1). The maximum total pore volume of the almond shells series ($0.36 \text{ cm}^3 \text{ g}^{-1}$) was attained for a holding time of 4 h (Table 2).

From the point of view of the intended application, post-combustion CO_2 capture, it is desirable to develop adsorbents with a high volume of micropores of narrow pore size, to maximise adsorption capacity and selectivity in the operation conditions (low partial pressure of CO_2) [23, 24]. The sample with the greatest micropore volume of the two series was obtained from olive stones by activation at 800°C for 6h ($0.48 \text{ cm}^3 \text{ g}^{-1}$). Among the almond shells series, the carbon activated for 4 h shows the greatest pore volume ($0.33 \text{ cm}^3 \text{ g}^{-1}$), with an average micropore size of 0.75 nm.

3.1.5. Sample screening: CO_2 uptake

The dynamic CO_2 adsorption capacity of the activated samples at atmospheric pressure was evaluated in pure CO_2 flow between 25 and 100°C using a thermogravimetric analyser. The amount of CO_2 adsorbed decreases with increasing temperature, as expected due to the exothermic nature of the physisorption process (the profiles of the adsorbed amount *versus* temperature can be found in the supporting information). At 25°C , the adsorption capacity of the carbons lies between 2.3 and 3.1 mmol g^{-1} , whereas at 100°C the amount of CO_2 that remains adsorbed falls to 0.7 - 0.9 mmol g^{-1} (see Tables 1 and 2). The samples that showed the highest CO_2 uptake at 25°C , 3.1 mmol g^{-1} , were the olive stones activated for 6 and 8 h. These carbons also present the highest total pore volume of the series (0.51 and 0.49 cc g^{-1} , respectively). However, the carbon with the highest uptake at 100°C , 0.9 mmol g^{-1} , is that obtained from the almond shells by activation for 4 h. Although this sample has lower pore volume (0.36 cc g^{-1}) than the aforementioned samples, its average micropore width is significantly narrower (0.75 nm vs. 1.28 - 2.45 nm). As the temperature increases, only the most energetic adsorption sites (in the present case the narrowest pores) remain occupied.

3.1.6. Carbon production scale up

Carbon production was scaled up using a larger reactor in order to obtain a sufficient amount of adsorbent to carry out fixed-bed adsorption studies. Holding time was set to 6 h for the olive stones, and to 4 h for the almond shells, in accordance with the sample screening results. The resulting carbons will be referred to as OS, and AS, respectively. The overall yields obtained at the larger scale, shown in Table 3, are in good agreement with the series obtained in the smaller reactor (see Tables 1 and 2). Likewise, the total pore volume and micropore volume of carbons OS and AS (Table 3) are very close to those obtained at the lower scale for the same holding time (Tables 1 and 2). The CO₂ uptake capacities at 25 °C and 100 °C, evaluated in the thermogravimetric analyser, shown in Table 3, are also in good agreement with those of Tables 1 and 2. These CO₂ uptakes are higher than those of commercial activated carbons evaluated in similar conditions [32].

3.2. Equilibrium of adsorption of pure CO₂ and N₂

Figures 2 and 3 and represent the adsorption isotherms of CO₂ at 0, 25 and 50 °C for carbon OS and AS, respectively. The shape of the adsorption isotherms is of Type I, although less steep than those of other adsorbents, like zeolite 13X. This implies that the adsorption capacity at low pressures is lower, but also that the adsorbent regeneration is easier by vacuum swing adsorption (VSA) processes.

As expected, an increase in temperature diminishes the amount of CO₂ adsorbed. Likewise, the adsorption capacity decreases with decreasing pressure. It is therefore important to assess the adsorption capacity at partial pressures of CO₂ that are generally encountered in flue gases (<30 kPa). Although other adsorbents with higher pore volumes can present higher CO₂ adsorption capacity at higher pressures, the CO₂ adsorption capacity of carbons OS and AS in these conditions is high compared to other carbon materials (see Table 4); it is above that of commercial activated carbons such as Calgon BPL [33], Norit R1 Extra [34], or Norit R 2030 CO₂ which is commercialised as a CO₂ adsorbent [29]. At 25 °C, the CO₂ adsorption capacity of carbons AS and OS is between that of Brightblack™ at 20 and 30 °C, which is a carbon adsorbent specifically developed by ATMI Inc. to maximise CO₂ adsorption [35]. The CO₂ adsorption capacity is also above that reported for high-surface-area carbon molecular sieves prepared from petroleum mesophase pitch (VR-5-M in Table 4), which not long ago were claimed to be the best result ever obtained for CO₂ adsorption with carbon-based materials [36]. Comparing carbons OS and AS, it can be seen that the adsorption capacity at 15 kPa of AS is above that of OS (Table 4). However, at atmospheric pressure, this trend is reversed (see Table 3 and Figures 2-3). The lower adsorption capacity at higher pressure is related to the

lower pore volume of AS; on the other hand, the narrower micropores of AS have a higher adsorption potential, which imparts higher adsorption capacity at lower pressures.

The adsorption isotherms of N_2 at 0, 25 and 50 °C for carbons OS and AS are shown in Figures 4 and 5, respectively. The shape of the N_2 adsorption isotherms is nearly linear: the amount of N_2 adsorbed increases linearly with pressure, indicating a weaker adsorbate-adsorbent interaction than that of CO_2 . It is important to highlight that the adsorption capacity of N_2 is significantly lower than that of CO_2 , as the ratio of the adsorption capacities for pure CO_2 and N_2 , is usually taken as an indicative of the equilibrium selectivity. However, selectivity is best assessed from multicomponent adsorption measurements, because the adsorption of a weaker adsorbate is reduced in the presence of a stronger adsorbate, as will be discussed later. The N_2 adsorption capacity of AS is lower than that of carbon OS. For post-combustion CO_2 capture applications, the lower the N_2 adsorption capacity the better, as this will improve the purity of the recovered CO_2 .

As can be seen from Figures 2-5, the Sips model describes satisfactorily the equilibrium of adsorption of pure CO_2 and N_2 in the temperature and pressure range studied. The best-fit parameters are shown in Table 5. Parameter n characterises the heterogeneity of the system; it takes a value close to unity for N_2 , but deviates from this value for CO_2 , indicating a higher degree of heterogeneity for the latter adsorbate. On comparing the two carbons under study, it can be seen that the values of n and Q are higher for AS than for OS; this is attributed to the narrower porosity of carbon AS.

As it has been shown in Figures 2-5, temperature strongly affects the equilibrium adsorption capacity at a given pressure. In an adsorptive separation process, the temperature is shifted during the adsorption step due to the exothermic nature of the adsorption process, and it is diminished during desorption, which is an endothermic process. This thermal effect tends to reduce the adsorber performance, as it reduces the equilibrium capacity during the adsorption step and increases the equilibrium capacity during the regeneration step. The extent of the temperature change is driven by the isosteric heat of adsorption, which is a critical variable for the design of an adsorptive separation process. Figure 6 represents the isosteric heat of adsorption of CO_2 and N_2 for carbons AS and OS as a function of loading. The isosteric heat of adsorption of CO_2 presents a soft downward trend with the amount of CO_2 adsorbed, which indicates a small degree of heterogeneity. For carbon adsorbents, this heterogeneity is usually related to the pore size distribution [37]; AS presents a slightly higher isosteric heat of adsorption of CO_2 at low loadings than OS due to its narrower pore size. However, the average

value of the isosteric heat of adsorption of CO₂ is similar for both samples: 27 kJ mol⁻¹. This value is significantly lower than those reported for Zeolite 13 X, 36-37 kJ mol⁻¹ [33, 38], or for several MOFs: 40-90 kJ mol⁻¹ [7], due to the weaker adsorption forces involved. The isosteric heat of adsorption of N₂ is nearly half that of CO₂: 15-16 kJ mol⁻¹, which is commonly attributed to its lower quadrupole moment. The isosteric heats of adsorption of CO₂ and N₂ are in good agreement with those reported for other carbon adsorbents: Calgon BPL (30 and 16 kJ mol⁻¹ for CO₂ and N₂, respectively) [33], BrightBlack™ (28-26 and 16 kJ mol⁻¹ for CO₂ and N₂, respectively) [35], *etc.*

The isosteric heat of adsorption predicted by the Sips model with the temperature dependence form as given by Equations 4 and 5, is expressed by [28]:

$$(\Delta H) = Q - (\alpha R_g T_0) n^2 \ln \left(\frac{c_p}{c_{ps} - c_p} \right) \quad (6)$$

The dependence of the isosteric heat of adsorption of CO₂ with loading as predicted by Equation 6 at 25 °C lies in between the behaviour previously observed for carbon OS and AS (Figure 6). For N₂ adsorption, the values predicted by the Sips model are in general in good agreement with those calculated directly from the experimental adsorption isotherms at 0, 25 and 50 °C, except at very low loadings, due to an intrinsic limitation of the model [28]. Other commonly used adsorption models, like Langmuir or Toth, present a greater deviation from the experimental data, hence the Sips model was considered to be more adequate for describing the equilibrium of adsorption of CO₂ and N₂ in the temperature and pressure range studied.

3.3. Fixed-bed adsorption experiments

To assess the performance of OS and AS under post-combustion conditions, dynamic experiments were carried out in the fixed-bed adsorption unit described in Section 2. The characteristics of the adsorption beds can be found in Table 6. Although the helium density of sample AS is slightly higher than that of OS, the particle and bed density of OS are greater than those of AS. The adsorber was filled to nearly its maximum volumetric capacity (maximum height 15 cm) for both samples, which implies that a lower loading of AS is possible on a mass basis.

Figure 7a represents the binary breakthrough curve of a mixture of 14 % CO₂ (balance N₂) at 30 °C and 120 kPa for carbon AS (the adsorption bed was initially full of helium). Two consecutive experimental runs are represented by empty and filled symbols (see the good

repeatability). N₂ reaches the adsorber outlet almost instantly (breakthrough time < 0.6 min). During nearly 5 min, all the incoming CO₂ is adsorbed, and a decarbonised effluent leaves the adsorber; *i.e.*, AS can *de facto* separate the CO₂ from a binary N₂/CO₂ stream with a partial pressure of CO₂ representative of post-combustion conditions. A roll-up can be observed in the N₂ curve (the molar flow rate of N₂ in the effluent is temporally greater than that fed to the column) due to the preferential adsorption of CO₂. Once equilibrium is attained, the molar flow rates of CO₂ and N₂ in the effluent equal those fed to the column. After 60 min, the completely saturated bed (in equilibrium with the feed) was regenerated by switching the feed gas to 60 sccm of helium (the temperature was kept constant at 30 °C during desorption). Figure 7b shows the desorption curves for CO₂ and N₂. As expected, due to the stronger nature of CO₂ adsorption, N₂ was more readily displaced by helium. Nevertheless, CO₂ is desorbed relatively easily, by simply purging the bed at 30 °C, without the need for heating, which is interesting from the point of view of the energy consumption of the final application. This is in good agreement with the moderate value observed for the isosteric heat of adsorption of CO₂. The stronger the adsorption (higher value of the isosteric heat of adsorption) the harder will be to regenerate the sorbent (higher energy consumption). The sorbed amount of each component was calculated by making a mass balance to the adsorber, subtracting the gas in the void space: 0.92 and 0.17 mmol g⁻¹ for CO₂ and N₂, respectively. Note that the N₂ adsorbed from the gas mixture is roughly half of the adsorption capacity for the pure component at the same partial pressure, while the adsorption capacity for CO₂ (strong adsorbate) is less influenced by the presence of N₂ (weak adsorbate).

It is common to define an equilibrium separation factor as:

$$\alpha_{AB} = \frac{x_A/y_A}{x_B/y_B} \quad (7)$$

where x and y refer to the molar fractions in the adsorbed and fluid phases at equilibrium [39]. The higher the separation factor, the higher the purity of the product that can be expected in an adsorption process [40]. Few studies give experimentally calculated selectivities from multicomponent adsorption experiments; the reported values are most frequently based on pure adsorption data, or in the best of cases, on IAST predictions. Moreover, comparison between different adsorbents needs to be carried out carefully as the separation factor varies with the experimental conditions (pressure, temperature, and composition of the gas phase). The CO₂-over-N₂ equilibrium separation factor of AS, calculated from the above presented multicomponent experiment, is 33. In the same conditions, the Sips adsorption model for the pure components, predicts a separation factor of 20, and the IAS theory, making use of the

Sips model for the pure components, gives 43. The pure component adsorption models do not consider competitive adsorption; hence the amount adsorbed is overestimated (especially in the case of the weak adsorbate), resulting in an underestimation of the real selectivity of the adsorbent. The difference observed between the separation factor calculated from the multicomponent experiment and that predicted by IAST may be attributed to: (1) intrinsic experimental error in the determination of the adsorbed amounts from the multicomponent mixture, (2) insufficient quality of the pure component equilibrium data, (3) limitation of the Sips adsorption model to reproduce the equilibrium of adsorption of the pure components, and/or (4) non idealities of the adsorbed phase [41]. In any case, the separation factor of AS can be considered high for a non-functionalised adsorbent. Recently, a separation factor of 44 has been reported for a K-N-doped carbon at 25 °C and 100 kPa for a mixture with 10 % CO₂ (balance N₂) [42]. However, the isosteric heat of adsorption of CO₂ of the latter material (40-60 kJ mol⁻¹) is also higher than that of the carbons presented here.

Experimental curves were simulated using Aspen Adsorption software assuming the Ideal Adsorption Solution Theory (IAST) to account for the competitive adsorption between CO₂ and N₂ and making use of the Sips model for the pure components. From Figure 7 it can be observed that the simulation satisfactorily reproduces the experimental adsorption and desorption curves. Axial dispersion is negligible due to the small dimension of the column (the curve obtained under the assumption of plug flow (not shown) is coincident with that obtained considering axial dispersion). The values of the overall mass transfer coefficients that reproduced the experimental data best were 0.2 s⁻¹ and 0.04 s⁻¹ for CO₂ and N₂, respectively. These values are relatively high, especially for CO₂, compared to the linear driving force parameters reported for commercial activated carbon Norit R 2030 CO₂ [43]. In fact, a sensitivity analysis showed that increasing the mass transfer coefficient of CO₂ above 0.2 s⁻¹ has no further effect on the shape of the simulated breakthrough curve for CO₂. A low overall mass transfer resistance is highly desirable for rapid swing processes. The effective overall mass transfer resistance can be estimated from the sum of the extra- and intraparticle mass transfer resistances [39]:

$$\frac{1}{k} = \frac{R_p}{3k_f} + \frac{R_p^2}{15\epsilon_p D_p} + \frac{r_0^2}{15\epsilon_p D_0} \quad (8)$$

where k is the overall effective mass transfer coefficient (s⁻¹), R_p is the particle radius, k_f is the external fluid film mass transfer coefficient, D_p is the pore diffusivity, ϵ_p is the particle porosity,

r_c is the crystal or micropore radius, K is a dimensionless Henry constant, and D_c is the intracrystalline or micropore diffusivity. Under most circumstances, intraparticle resistance is of greater importance than external film resistance in determining the overall mass transfer rate [39]. If the film coefficient is estimated through the Wakao and Funazkri correlation [44], the first term of Equation 8 becomes 0.02 s (reciprocal time constant: 45 s^{-1}); *i.e.* the external mass transfer is not governing the overall rate. The pore diffusivity can be estimated from the Knudsen (D_K) and molecular diffusivities (D_m) using the Bosanquet equation: $1/D_p = \tau (1/D_m + 1/D_K)$, where τ is a tortuosity factor. The molecular diffusivities of CO_2 and N_2 in helium were estimated from the Chapman-Enskog theory [45], and the Knudsen diffusion was calculated for an average pore size of 1.84 nm (estimated from N_2 adsorption at -196°C). Assuming a tortuosity factor of 4, the pore diffusivity is of the order of $1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$, which leads to a second term of Equation 8, related to the mass transfer resistance in the macropores, of the order of 0.6-0.8 s, which is one order of magnitude higher than the extraparticle resistance term. Diffusion in the micropores, which have an average size close to that of the molecular size of N_2 and CO_2 , is probably the rate limiting mechanism. Andrieu and Smith studied the adsorption rate parameters of CO_2 in Calgon BPL activated carbon and found that its apparent time constant for micropore diffusion was 0.106 s^{-1} at 30°C [46]. This parameter is not far from the overall mass transfer coefficient found for AS. Bae and Lee studied the apparent time constants for N_2 and CO_2 on the carbon molecular sieve CMS-T3A from Takeda (average micropore diameter 0.4 nm) between 20 and 40°C , and found that the relative order was $\text{CO}_2 > \text{N}_2$, in good agreement with our experimental results; the larger quadrupole moment and polarizability of CO_2 compared to that of N_2 leads to stronger molecular interactions and faster sorption rates [47]. This trend in the magnitude of the mobility parameters ($\text{CO}_2 > \text{N}_2$) has been observed for other molecular sieving carbons [48].

To assess the effect of adsorption temperature, the breakthrough curves were obtained at 50°C , which is a plausible temperature for a flue gas exiting a desulfurisation unit. The corresponding curves for CO_2 and N_2 are shown in Figure 8. The CO_2 breakthrough time is reduced due to the lower adsorption capacity at the higher temperature, but the separation efficiency is preserved: for nearly 4 min, a CO_2 -free effluent is produced. Figure 8b shows the desorption curves of CO_2 and N_2 at 50°C . Not surprisingly, CO_2 desorbs faster at the higher temperature; the CO_2 content of the effluent falls below 1 % after only 8 min. The total amounts of CO_2 and N_2 desorbed are 0.61 and 0.13 mmol g^{-1} , respectively, which leads to an experimental equilibrium separation factor of 30. The IAST predictions at 50°C leads to a

separation factor of 36, which is close to the experimental value. The selectivity of sample AS is not substantially affected by the increase in the adsorption temperature from 30 to 50 °C.

The breakthrough curves at 50 °C were also simulated using Aspen Adsorption; the values of the overall mass transfer coefficients that reproduced the experimental data best were 0.2 s^{-1} and 0.06 s^{-1} for CO_2 and N_2 , respectively. The simulated adsorption and desorption curves for N_2 reproduce the experimental data fairly well. The overall mass transfer coefficient for N_2 increases with increasing temperature, as expected. In fact, it follows an Arrhenius dependence on temperature, with a calculated activation energy of 17 kJ mol^{-1} , that is close to the isosteric heat of adsorption. This is expected of microporous diffusion control [49]. The simulation results present a greater deviation from the experimental CO_2 curves. A better approximation was not possible using the linear driving force (LDF) approximation, as increasing the overall mass transfer coefficient of CO_2 above 0.2 s^{-1} has no further effect on the shape of the simulated curve. A better agreement was achieved by using a model that solves the material balance for the particle more rigorously (Particle MB; Figure 8). A constant effective adsorbed phase diffusion coefficient for N_2 of $4 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (equivalent to an overall mass transfer coefficient of 0.06 s^{-1} assuming micropore diffusion control); and of $4 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$ for CO_2 were assumed. Again, it was observed that increasing the value of the adsorbed phase diffusivity for CO_2 above this value has no significant effect on the shape of the CO_2 curve. Mass transfer resistance does not appear to be rate-limiting for CO_2 in the temperature range studied.

Figure 9 shows the CO_2 and N_2 breakthrough curves at 50 °C for carbon OS. The CO_2 breakthrough time is roughly 1 min higher than that of AS, mainly due to its higher bed density. On a mass basis, the CO_2 adsorption capacity of OS in the evaluated experimental conditions, 0.58 mmol g^{-1} , is slightly below that of AS. The experimental equilibrium separation factor (20) is also lower than that of AS in the same experimental conditions evaluated. The higher selectivity of AS is attributed to its narrower porosity. The separation factor of OS calculated by IAST (18) is very close to the experimental value. In the present case, the simulation satisfactorily describes the experimental data making use of the LDF approximation, with an overall mass transfer coefficient of 0.2 s^{-1} for CO_2 and 0.07 s^{-1} for N_2 . The mass transfer coefficient for N_2 is slightly higher than that used to carry out the simulation with carbon AS, in good agreement with the wider micropore size of sample OS (lesser resistance to mass transfer). As before, mass transfer does not seem to be the rate-limiting mechanism for CO_2 (increasing the mass transfer coefficient above 0.2 s^{-1} has no further effect on the shape of the simulated breakthrough curve for CO_2).

4. Conclusions

Low cost and sustainable adsorbents were produced from two renewable agricultural residues, olive stones and almond shells, by single-step activation with CO₂. The activation conditions were optimised to maximise the micropore volume of the final carbons with a narrow micropore size, adequate for CO₂ adsorption at low pressures. Optimal conditions were used to scale up the carbon production process.

The optimised adsorbents showed a high CO₂ adsorption capacity (up to 4.8 mmol g⁻¹ at 101 kPa and 0 °C). The CO₂ adsorption capacity at 15 kPa, a partial pressure that could be encountered in the flue gases entering a post-combustion capture unit, is 1.0-1.1 mmol g⁻¹ at 25 °C and 0.6-0.7 mmol g⁻¹ at 50 °C. This adsorption capacity for CO₂ is among the highest reported for carbon materials. The adsorption capacity for N₂ is substantially lower than for CO₂ (factor above 1:7). The Sips adsorption model can be used to describe the adsorption of pure CO₂ and N₂ between 0 and 50 °C up to 120 kPa on the adsorbents selected.

Multicomponent experiments, carried out in a fixed bed unit, demonstrated that the adsorbents are capable of separating a binary stream containing 14 % CO₂ (balance N₂) at 50 °C, which is the temperature of flue gases after a desulfuration unit. Moreover, the adsorbents showed fast adsorption and desorption kinetics, which is necessary for their implementation in rapid swing adsorption processes, and they are easily regenerated, which will reduce the cost of the regeneration step.

The binary CO₂/N₂ adsorption and desorption experiments demonstrated that the amount of N₂ adsorbed is substantially reduced in the presence of CO₂ compared to pure component adsorption data, while the amount of CO₂ adsorbed (strong adsorbate) is little influenced by the presence of N₂ (weak adsorbate). A fixed-bed adsorption model based on a lumped overall mass transfer resistance making use of the linear driving force approximation, and using IAST to account for competitive adsorption, adequately describes the adsorption kinetics of N₂. Calculated coefficients for the macropore and the external film resistances showed that these are not determining the overall mass transfer rate. Moreover, the overall mass transfer coefficient for N₂ showed an Arrhenius dependence with temperature, which is indicative of micropore diffusion control. A sensitivity analysis was carried out increasing the overall mass transfer coefficient for CO₂: mass transfer resistance does not seem to be the rate-limiting step for this adsorbate.

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Tables

Table 1. Effect of holding time on overall yield, textural development, and CO₂ uptake of olive stones activated at 800 °C

Holding time (h)	Overall yield (%)	N ₂ adsorption at -196 °C				CO ₂ uptake (mmol g ⁻¹)	
		S_{BET} (m ² g ⁻¹)	V_p (cc g ⁻¹)	$V_{\text{DR-N}_2}$ (cc g ⁻¹)	L_{N_2} (nm)	25 °C	100 °C
0.5	25	539	0.22	0.21	0.59	2.4	0.7
1.0	23	623	0.26	0.24	0.58	2.5	0.7
1.5	22	687	0.30	0.26	0.60	2.7	0.7
2.0	20	774	0.32	0.30	0.60	2.7	0.7
4.0	18	956	0.40	0.37	0.93	2.9	0.7
6.0	10	1215	0.51	0.48	1.28	3.1	0.8
8.0	7	1063	0.49	0.41	2.45	3.1	0.8

Table 2. Effect of holding time on overall yield, textural development, and CO₂ uptake of almond shells activated at 750 °C

Holding time (h)	Overall yield (%)	N ₂ adsorption at -196 °C				CO ₂ uptake (mmol g ⁻¹)	
		S_{BET} (m ² g ⁻¹)	V_p (cc g ⁻¹)	$V_{\text{DR-N}_2}$ (cc g ⁻¹)	L_{N_2} (nm)	25 °C	100 °C
0.5	25	451	0.22	0.18	0.67	2.3	0.8
1.0	20	540	0.24	0.21	0.63	2.5	0.8
1.5	NA	626	0.27	0.25	0.65	2.5	0.8
2.0	17	721	0.32	0.28	0.70	2.5	0.8
4.0	9	862	0.36	0.33	0.75	2.7	0.9
6.0	5	613	0.26	0.25	1.70	2.6	0.8

Table 3. Overall yield, textural development, and CO₂ uptake of the carbons obtained from olive stones (OS) and almond shells (AS) at higher scale

Sample	Temperature (°C)	Holding time (h)	Overall yield (%)	N ₂ adsorption at -196 °C				CO ₂ uptake (mmol g ⁻¹)	
				S_{BET} (m ² g ⁻¹)	V_p (cc g ⁻¹)	$V_{\text{DR-N}_2}$ (cc g ⁻¹)	L_{N_2} (nm)	25 °C	100 °C
OS	800	6	10	1113	0.51	0.45	0.94	3.0	0.7
AS	750	4	7	822	0.37	0.31	0.86	2.7	1.0

Table 4. CO₂ adsorption capacity of carbonaceous solid adsorbents

Sorbent	Temperature (°C)	Pressure (kPa)	Capacity (mmol g ⁻¹)	method	reference
BPL	25	15	0.70	volumetric	[33]
Norit AC 1 Extra	25	15	0.54	gravimetric	[34]
Brightblack™	20	15	1.21	volumetric	[35]
Brightblack™	30	15	0.89	volumetric	[35]
VR-5-M	25	15	0.89	manometric	[36]
Norit R2030 CO2	25	15	0.84	volumetric	This work
OS	25	15	1.02	volumetric	This work
AS	25	15	1.08	volumetric	This work
VR-5-M	50	15	0.43	manometric	[36]
Norit R2030 CO2	50	15	0.47	volumetric	This work
OS	50	15	0.58	volumetric	This work
AS	50	15	0.68	volumetric	This work

Table 5. Sips parameters for the adsorption of CO₂ and N₂ on carbons OS and AS between 0 and 50 °C

	OS		AS	
	CO ₂	N ₂	CO ₂	N ₂
C_{H_2}	15.27	3.62	10.74	3.34
b_0	0.0029	0.0022	0.0028	0.0017
n	1.562	1.058	1.883	1.053
Q	19.804	13.414	21.146	11.522
α	0.5461	0.4045	0.3483	0.4751

Table 6. Adsorption bed characteristics

Sample	OS	AS
Mass of adsorbent (g)	2.8	2.0
Bed density (kg m ⁻³)	295	205
Particle density (kg m ⁻³) ^a	536	517
Solid density (kg m ⁻³) ^b	1969	1996
Bed void	0.45	0.60
Particle void	0.73	0.74

^aDetermined by mercury intrusion at 0.1 MPa; ^bDetermined by helium pycnometry

Figures

Figure 1. Comparison of mass loss profiles of raw olive stones (blue lines) and almond shells (red lines) during heating at 15 °C min⁻¹ in CO₂ flow.

Figure 2. CO₂ adsorption isotherms of olive stone-based carbon (OS) at 0, 25 and 50 °C.

Figure 3. CO₂ adsorption isotherms of almond shell-based carbon (AS) at 0, 25 and 50 °C.

Figure 4. N₂ adsorption isotherms of olive stone-based carbon (OS) at 0, 25 and 50 °C.

Figure 5. N₂ adsorption isotherms of almond shell-based carbon (AS) at 0, 25 and 50 °C.

Figure 6. Isothermic heat of adsorption of CO₂ and N₂ on carbons derived from almond shells (red squares) and from olive stones (blue diamonds). Symbols represent the values calculated through the Clausius-Clapeyron equation from the adsorption isotherms at 0, 25 and 50 °C, and solid lines represent the prediction of the Sips model.

Figure 7. Evolution of CO₂ and N₂ molar flow rates at the adsorber outlet during: (a) the breakthrough of a binary mixture (14 % CO₂, balance N₂) at 30 °C and 1.2 bar over a bed of AS initially full of helium, and (b) desorption of previously adsorbed CO₂ and N₂ by purging the bed with helium. Symbols represent the experimental data, and solid lines the simulation results.

Figure 8. Evolution of CO₂ and N₂ molar flow rates at the adsorber outlet during: (a) the breakthrough of a binary mixture (14 % CO₂, balance N₂) at 50 °C and 1.2 bar over a bed of AS initially full of helium, and (b) desorption of previously adsorbed CO₂ and N₂ by purging the bed with helium. Symbols represent the experimental data, and solid lines the simulation results.

Figure 9. Evolution of CO_2 and N_2 molar flow rates at the adsorber outlet during: (a) the breakthrough of a binary mixture (14 % CO_2 , balance N_2) at 50 °C and 1.2 bar over a bed of OS initially full of helium, and (b) desorption of previously adsorbed CO_2 and N_2 by purging the bed with helium. Symbols represent the experimental data and solid lines the simulation results.