Cherry stones-based activated carbons as potential adsorbents for CO₂/CH₄ separation: Effect of the activation parameters

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Abstract

A low-cost biomass, cherry stones (CS), was used as carbon precursor to synthesize two activated carbons to be used for CO₂/CH₄ separation. Single-step activation with two activating agents, carbon dioxide and steam, was used. The activation conditions that maximize the CO₂ adsorption capacity by the adsorbents at 25 °C and atmospheric pressure were determined by response surface methodology (RSM). The optimum values were 885 °C and 12% of solid yield when activating with carbon dioxide, but 850 °C and 15.3% of solid yield when activating with steam. Heating rate did not show a significant effect on the CO₂ uptake. CO₂ adsorption capacity values up to 11.45 and 10.56 wt.% were achieved under such conditions using carbon dioxide and steam as activating agents, respectively. Carbon dioxide activation promoted the development of microporosity, whereas both micropores and mesopores were developed during steam activation. The CO₂/CH₄ separation performance at 3 bar of the optimum adsorbents indicated that both cherry stones-based activated carbons could have great potential as CO₂ adsorbents for CO₂/CH₄ separation. The adsorbent activated with carbon dioxide, CS-CO₂, showed a slightly higher adsorption capacity, but the steam activated sample, CS-H₂O, had an enhanced selectivity to separate CO₂ from CO₂/CH₄ binary mixtures.

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1 INTRODUCTION

Biogas is produced from the decomposition of organic wastes, and is rich in CH₄ (35-75 vol.%). Its release into the atmosphere largely contributes to greenhouse gas concentration. However, the energetic content of the biogas is high (higher heating value of 15-30 MJ Nm⁻³) and its exploitation involves significant revenues or avoided costs.¹

CO₂ is present in the biogas in large quantities (almost balanced to the percentage of CH₄), and as it is an inert gas in terms of combustion, it decreases the energetic content of the biogas. The main technology used for enriching biogas in CH₄ by means of CO₂ separation is pressure swing adsorption (PSA) on zeolites, due to their high selectivity towards CO₂. Nevertheless, activated carbons (ACs) can be promising materials for CO₂/CH₄ separation due to their high adsorption capacity at atmospheric pressure, hydrophobic character, significant lower cost than zeolites, high surface area and amenability to pore structure modification and surface functionalization.² Moreover, a lower amount of energy is needed to regenerate activated carbons compared to zeolites. Some of the requirements that need to fulfil the ACs in order to be competitive materials for CO₂/CH₄ separation purposes are availability, high stability, ease of regeneration and low cost, as well as high CO₂ selectivity and adsorption capacity. Carbon adsorbents can be obtained at low cost if a renewable, relatively abundant and globally available source, such as biomass, is used as precursor material.

The production of carbon adsorbents from biomass precursors can involve physical or chemical activation to develop the porosity.³ The adsorption capacity of an

AC is mainly dependent on its pore structure. In the present work, physical activation was selected due to its lower energy consumption and processing time, as well as it has a lower environmental impact when using CO₂, H₂O or air as activating agent. Physical activation is generally carried out in a two-step procedure: carbonization and activation. Single-step activation has been less explored, although good adsorption characteristics for removal of NO₂ from air or pollutants from water have been reported in literature after biomass activation by a single-step procedure using CO₂ or steam as activating agents.⁴⁻⁷ Single-step activation was therefore selected in the present work for preparing cherry stones-based activated carbons.

Every carbon precursor requires specific activation conditions, and so an increase in the activation degree could only be justified if a significant improvement in the adsorption capacity of the adsorbent was observed. Therefore, CO₂ adsorption on the activated carbons prepared in the present work was optimized in relation to temperature, heating rate and solid yield during the single-step activation by means of response surface methodology (RSM). RSM is a statistical technique which has lately been applied in research related with CO₂ capture to evaluate the effects of several factors and determine the optimum conditions for the studied process.^{8,9} It uses the design of experiments and the multiple regression analysis to model the relationship between several independent variables and a response variable.¹⁰

The commercial synthesis of activated carbons is currently demanding cheap, easily accessible and widely available precursors. An agricultural by-product, such as cherry stones (CS), is abundant in Spain, especially in the regions of Extremadura and Aragón, from the industrial production of Kirsch (cherry brandy) and jam. The cherry stones could be recycled by means of the production of activated carbons, since they

constitute a source of renewable carbon with a low cost. In addition, they are suitable for preparing microporous activated carbons due to their low ash content. To the best of our knowledge, few studies have been published on the preparation of activated carbons from cherry stones, which were synthesized by conventional two-step activation and they were characterized and evaluated for adsorbing gases such as NO₂ or H₂S and liquid impurities.¹¹⁻¹⁴ However, studies on one-step CO₂ or steam activation of cherry stones have not been reported in literature. Therefore, in the present work two microporous activated carbons were for the first time prepared from cherry stones by single-step activation with carbon dioxide and steam for application in CO₂/CH₄ separation. CO₂ adsorption on these adsorbents was optimized in relation to the activation conditions (temperature, heating rate and solid yield) by means of RSM. Afterwards, two activated carbons were produced on a larger scale using the resulting optimum activation conditions and were texturally characterized. The performance to separate CO₂ from CO₂/CH₄ binary mixtures, representative of biogas streams, was evaluated.

2 EXPERIMENTAL

2.1 Single-step activation with CO₂ or steam

A low-cost biomass, cherry stones (CS), was used as starting material. Cherry stones were ground and sieved, and samples with a particle size between 1 and 3 mm were selected. The proximate and ultimate analyses of the raw material are collected in Table 1. The single-step activation with carbon dioxide or steam was carried out in a Setaram TAG24 thermobalance, methodology previously validated in our laboratory.¹⁵ Accordingly, in order to choose the activation temperature range, non-isothermal mass loss profiles of raw CS under carbon dioxide and steam up to 1000 °C were conducted

(data not shown). The temperature of commencement of mass loss, after the loss of moisture and volatile matter, was taken as the minimum activation temperature. Thus, a range of activation temperature of 750-950 °C was selected for the subsequent statistical study with both activating agents.

Given that single-step activation does not include a preliminary carbonization step, the term “solid yield” instead of “burn-off degree” was preferred in the present work. The solid yield was calculated by dividing the mass of the resulting activated carbon by the initial mass of the dried precursor. Samples of approximately 40 mg were used. In the case of the carbon dioxide activated adsorbents, the cherry stones samples were physically activated in a 100 mL min⁻¹ stream of CO₂, whereas for the steam activated carbons, the activation was carried out under a 100 mL min⁻¹ stream containing 35 vol.% of H₂O (balance N₂). Prior to activation the samples were dried at 100 °C under an inert atmosphere of N₂. The duration of the activation process was dependent on the solid yield targeted in each experiment.

The preparation of the two optimum activated carbons on a larger scale following the experimental conditions determined from the above study was carried out in a vertical furnace from Carbolite. Samples of approximately 10 g were activated under the same conditions used in the thermobalance.

2.2 Response surface methodology

Response surface methodology was used to optimize the activation variables that maximize the CO₂ adsorption capacity at 25 °C and atmospheric pressure of each cherry stones-based activated carbon. Three independent variables were evaluated: activation temperature (*T*) between 750 and 950 °C, heating rate (*HR*) between 10 and 20 °C min⁻¹ and solid yield after activation (*Y*) between 7 and 17% for CS activated with

carbon dioxide and between 7 and 22% for CS activated with steam. The response or dependent variable, which is measured during the experiments, was the CO₂ uptake.

The experimental design selected in this study was the central composite design (CCD), which consists of the following parts: (1) a full factorial design; (2) a star design in which experimental points are at a certain distance, α , from its centre and (3) a replicated central point. The α -value depends on the number of variables, k , and can be calculated by $\alpha=2^{k/4}$; for three variables, it is 1.682. The CCD design involved 20 experiments, including eight factorial points (2^3 full factorial design), six axial points and six replicates of the centre of the design. The experiments were conducted in a random order. Prior to the application of RSM, the independent variables were coded in dimensionless values so that variables with different units or of different orders of magnitude could be compared. The coded (in parentheses) and the decoded values of the independent variables (T , HR and Y), together with the experimental results obtained for the response variable (CO₂ uptake) are shown in Table 2 for the carbon dioxide activated-CS and steam activated-CS adsorbents, respectively.

The experimental data collected from CCD for the three independent variables, x_1 (T), x_2 (HR) and x_3 (Y), were mathematical-statistically fitted to the following second-order polynomial model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \varepsilon \quad (1)$$

where y is the response variable; β_0 is the constant term; β_1 , β_2 and β_3 are the coefficients of the linear parameters; β_{11} , β_{22} and β_{33} are the coefficients of the quadratic parameters; β_{12} , β_{13} , β_{23} and β_{123} are the coefficients of the interaction parameters and ε is the residual associated with the experiments. The experimental data were fitted to Eq. (1)

by multiple regression analysis (least squares) and the β coefficients that generate the lowest possible residual were determined. The fitness of the quadratic model to the experimental data was evaluated by analysis of variance (ANOVA) and lack-of-fit tests. A model was considered to fit the experimental data well when it showed a significant regression (p -value<0.05 to a confident level of 95%) and a non-significant lack of fit (p -value>0.05 to a confident level of 95%). The accuracy of the fitted polynomial model was expressed by the coefficient of determination R^2 and by Adj- R^2 , which penalizes the statistic R^2 as extra variables are included in the model. The absolute average deviation (AAD) was also calculated in order to check the accuracy of the model. ADD describes the deviations between the experimental and calculated values. It must be as small as possible and is calculated as follows:¹⁶

$$\text{AAD (\%)} = 100 \left[\sum_{i=1}^n \left(\frac{|y_{i,\text{exp}} - y_{i,\text{calc}}|}{y_{i,\text{exp}}} \right) \right] / n \quad (2)$$

where $y_{i,\text{exp}}$ and $y_{i,\text{calc}}$ are the experimental and calculated responses, respectively, and n is the number of experiments. The statistical analyses were carried out using SPSS Statistics 21.0 software.

To visualize the combined effects of two factors on the response, the three-dimensional plot of the model, i.e., response surface plot, was obtained. The two-dimensional display of the surface plot generates the contour plot, where the lines of constant response are drawn on the plane of the two independent variables. Response surface and contour plots were generated using the SigmaPlot 10.0 software. Then, the optimum values for each independent variable that would produce the best response in the experimental region under study were determined.

2.3 CO₂ uptake

The CO₂ capture capacity of the adsorbents was evaluated in a Setaram TAG24 thermogravimetric analyser at 25 °C and atmospheric pressure. Prior to the adsorption measurements, the samples (approximately 40 mg) were dried in situ. Afterward, a CO₂ adsorption test was conducted under a CO₂ flow rate of 100 mL min⁻¹ at 25 °C up to constant mass. The maximum CO₂ uptake at atmospheric pressure and 25 °C was evaluated from the increase in mass experienced by the sample and it was expressed in terms of mass of CO₂ per mass of dry adsorbent.

2.4 Textural characterization of the optimum activated carbons

The porosity in the optimum cherry stones-based ACs was determined by means of physical adsorption of N₂ at -196 °C and CO₂ at 0 °C in volumetric devices from Micromeritics. This allows the assessment of the porosity in the samples from the mesopores (sizes between 2 and 50 nm) down to the narrowest micropores (sizes less than 0.7 nm). The usefulness of both adsorptives to characterize the porosity of carbon materials has been previously reported.¹⁷ Moreover, considering the wide range of micropore size distributions that could be achieved during physical activation of a carbonaceous precursor, the combination of the two adsorptives is critical to tailor the characteristics of the AC for a specific application.

The apparent surface area was calculated from the N₂ isotherms using the Brunauer-Emmett-Teller equation (S_{BET})¹⁸ in the relative pressure range 0.01-0.1, whereas the total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. It is known that the CO₂ capture performance of carbon materials mainly involves the microporosity in the samples, so the Dubinin-Radushkevich (D-R) equation¹⁹ was used to estimate the micropore volume, W_0 , and the characteristic energy, E_0 , as realized by the corresponding molecular probe, N₂ or

CO₂. The average micropore width, L_0 , of the locally slit-shaped micropores is related to the characteristic energy by means of the Stoeckli-Ballerini relation²⁰, as follows:

$$L_0 \text{ (nm)} = 10.8 / (E_0 \text{ (kJ mol}^{-1}\text{)} - 11.4) \quad (3)$$

In addition, the micropore volume corresponds to $W_0 = (S_{\text{mic}}/2) L_0$, assuming a slit-shaped geometry and, consequently, the surface area of the micropore walls can be estimated by the geometrical relation:²¹

$$S_{\text{mic}} \text{ (m}^2 \text{ g}^{-1}\text{)} = 2000 W_0 \text{ (cm}^3 \text{ g}^{-1}\text{)} / L_0 \text{ (nm)} \quad (4)$$

The micropore size distributions in the range of 0.3-1 nm were estimated by means of the Non Local Density Functional Theory (NLDFT) on a slit pore carbon model applied to the CO₂ adsorption isotherms.²²

2.5 Adsorption and separation of CO₂/CH₄ tests on the optimum activated carbons

The adsorption isotherms of pure CO₂ and CH₄ of the cherry stones-based ACs prepared under the optimum activation conditions were measured up to 10 bar at 30 °C in a high pressure magnetic suspension balance (Rubotherm-VTI). Details on the set-up and the experimental procedure can be found elsewhere.²³ The absolute amounts of CO₂ and CH₄ adsorbed over the pressure range tested were estimated following the procedure described in García *et al.*²⁴

The experimental CO₂ and CH₄ adsorption isotherms of the cherry stones-based ACs were fitted to the Sips model according to the following expression:

$$q = q_s \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \quad (5)$$

where q represents the concentration of the adsorbed specie and q_s the saturation capacity, P the pressure of the adsorptive and b the affinity constant. The parameter n shows the heterogeneity of the system and its value is usually greater than unity;

therefore, the larger the value of n , the more heterogeneous is the system. The fitting of the experimental data to the Sips model was conducted by means of the *Solver Excel* tool assuming q_s and n to be equal for both CO₂ and CH₄ and departing from values of q_s and n of 1 and b_{CO_2} and b_{CH_4} of 0. The goodness of the fit was evaluated on the basis of the minimum squared relative error (*SRE*) as given by the following expression:

$$SRE(\%) = \sqrt{\frac{\sum_i [(q_{\text{exp},i} - q_{\text{mod},i})/q_{\text{exp},i}]^2}{N-1}} \times 100 \quad (6)$$

where $q_{\text{exp},i}$ and $q_{\text{mod},i}$ are the experimental and Sips-predicted adsorbed amounts, respectively, and N is the total number of experimental data points.

Using the fitted parameters from the pure component adsorption data, the adsorption data from a binary mixture of CO₂ and CH₄ may be predicted by an extended Sips model, similarly to the extended Langmuir equation for multicomponent adsorption. Rudziński *et al.*²⁵ stated that the application of the Ideal Adsorbed Solution Theory (IAST) with the concept of hypothetical pure-component pressure for normal activated carbons results in the following equation:

$$q_i = \frac{q_s b_i y_i P \left(\sum_{k=1}^N b_k y_k P \right)^{(1/n)-1}}{1 + \left(\sum_{k=1}^N b_k y_k P \right)^{1/n}} \quad (7)$$

Eq. (8) stands for the Sips multicomponent model where i represents the species for which the isotherm q_i is being evaluated, y is the mole fraction of the corresponding component (denoted by subscript i or k) in the gas phase, and N is the total number of components in the gas mixture.

3 RESULTS AND DISCUSSION

3.1 Effect of the activation parameters on CO₂ adsorption capacity of activated carbons: Response surface methodology

Table 3 shows the results of fitting Eq. (1) to the experimental data of both activated carbons, carbon dioxide activated-CS and steam activated-CS, by multiple regression analysis and those obtained from evaluating the fitness of the model by means of ANOVA, together with the R^2 , Adj- R^2 and AAD values. The coefficient values of the polynomial models presented in Table 3 are coded coefficients. Thus comparison of these values for a given material gives information of the relative influence of each independent variable on the response. The ANOVA tests showed that the models for the CO₂ capture capacity obtained were statistically significant to a 95% level of confidence (p -value<0.05), whereas their lack of fit was found to be statistically non-significant to a 95% confidence level (p -value>0.05). Table 3 also shows which terms of the models are statistically significant to a 95% confidence level (p -value<0.05); those that were not statistically significant (p -value>0.05) were later eliminated in the final models. The variable HR does not present a statistically significant effect on the CO₂ capture capacity for any studied material, CO₂ or steam activated. Lua and Guo⁴ prepared activated carbons from oil palm stones by one-step CO₂ activation and they also found that the heating rate had no significant effect on the porosity development of the adsorbents. On the contrary, Yang *et al.*⁵ observed very slight increases in the texture development when heating rate was raised from 5 to 10 °C min⁻¹.

No interaction effects between T , HR and Y were detected in the experimental region under study, since the $T \cdot HR$, $T \cdot Y$, $HR \cdot Y$ and $T \cdot HR \cdot Y$ interaction terms in the models proved to be statistically non-significant to a 95% confidence level (p -

value>0.05), as it is shown in Table 3. Once the non-significant terms were eliminated from the models, the coded coefficient values were decoded in order to obtain the polynomial equations that address the response variables as a function of the actual independent variables. The models obtained for both activated carbons were the following:

$$\text{CO}_2 \text{ uptake}_{\text{carbon dioxide activated-CS (wt.\%)}} = -60.71300 + 0.15307 T + 0.73377 Y - 0.00009 T^2 - 0.03057 Y^2 \quad (9)$$

$$\text{CO}_2 \text{ uptake}_{\text{steam activated-CS (wt.\%)}} = -23.07866 + 0.06211 T + 0.94793 Y - 0.00004 T^2 - 0.03103 Y^2 \quad (10)$$

Fig. 1 represents the response surface and contour plots for the CO₂ capture capacity as a function of the significant independent variables, i.e., activation temperature and solid yield, for carbon dioxide activated-CS (Fig. 1a) and steam activated-CS (Fig. 1b). For both activated carbons, the curve-shaped response surface and contour plot isolines clearly indicate that a maximum response is achieved in the temperature and solid yield ranges studied, i.e., within the experimental region considered.

For the carbon dioxide activated-CS adsorbent (Fig. 1a), the highest CO₂ capture capacity (11.45 wt.%) was achieved at an activation temperature of 885 °C and a solid yield of 12%. This means that as the activation temperature increases from 750 °C, a marked increase in the CO₂ capture capacity is observed up to a maximum value. However, when the activation temperature increases above 885 °C, a slight decrease is observed in the CO₂ uptake up to 950 °C. An optimum solid yield can be also identified, although this parameter has a lower influence on the response. This is indicated by the lower coded coefficient for the *Y* term compared to that for the *T* term in Table 3.

Therefore, temperature is the most influential activation parameter on the CO₂ uptake of the carbon dioxide activated-CS adsorbent. This fact suggests that an increase in the activation temperature (up to 885 °C) is more efficient in raising the CO₂ capture capacity of the synthesized adsorbent than a similar decrease in coded units in the solid yield between 17 and 12%.

For the steam activated-CS activated carbon (Fig. 1b) the highest CO₂ capture capacity (10.56 wt.%) was however attained at an activation temperature of 850 °C and a solid yield of 15.3%. Even though an optimum activation temperature can be observed for steam activated-CS, this parameter shows little influence on the response. Thus, the CO₂ capture capacity is only slightly affected by temperature at a given solid yield. In this case, as the solid yield decreases from 22%, a strong increase in the CO₂ uptake is observed up to a maximum value. Nevertheless, when the solid yield decreases below 15.3%, the CO₂ adsorption capacity rapidly drops. The solid yield is therefore the most influential activation parameter on the CO₂ capture capacity for the steam activated-CS adsorbent. This can also be inferred from the higher coded coefficient of the *Y* term compared to that of the *T* term in Table 3. From all these results, it is also confirmed that, in the experimental region studied, the activation parameters do not similarly influence the capture capacity of both ACs.

Higher solid yields are the result of lower activation degrees. Thus, the existence of a maximum in the CO₂ capture capacity indicates that at low temperatures and activation degrees (high solid yields) the extent of the activation is too weak and hence the microporosity development in the materials is poor. However, when temperature and activation degree are increased (lower solid yields), the CO₂ capture capacity rises up to the maximum value. Then, a further increase in temperature and activation reduce

the microporosity in the samples due to the collapse of adjacent pore walls; this results in lower CO₂ uptakes.

The highest CO₂ uptake at atmospheric pressure and 25 °C corresponded to the carbon dioxide activated-CS adsorbent, which reached 11.45 wt.%, but a relatively high CO₂ uptake value (10.56 wt.%) was also attained by steam activated-CS. This could indicate that a higher micropore volume might be expected by means of CO₂ activation compared to steam, since it has been shown that adsorbents with high volumes of micropores in the narrow micropore size domain are required to maximize CO₂ adsorption capacity at low pressures and room temperature.^{26,27}

When steam is used as activating agent, the maximum CO₂ uptake is achieved at a temperature of 850 °C, indicating that the optimum textural development for this application may be reached; higher temperature values would lead to extensive gasification, ruining the porosity created and hence reducing the adsorption capacity. However, when a less reactive gas such as carbon dioxide is used as activating agent, activation proceeds slower and higher temperatures, 885 °C in the present study, are needed to reach the optimum textural development and consequently the maximum CO₂ uptake. Moreover, a longer activation time (lower solid yield) is also needed to reach the optimum development of the carbon porosity when activating with carbon dioxide. In single-step activation of biomass residues under oxygen atmospheres, it has been found that the combination of a less reactive activating agent (i.e., air with a reduced oxygen content) together with a higher activation temperature further develops the narrowest pores, those with greater adsorption potential and therefore being more effective for adsorbing CO₂ at ambient conditions.²⁸ On the other hand, Gergova and Eser⁷ highlighted that the evolution of porosity is much more difficult to control during

activation with steam than that with CO₂ due to the higher reactivity of the solid carbons under steam conditions compared to CO₂. Therefore, the lower reactivity of the CS precursor under a carbon dioxide atmosphere compared to steam has probably influenced the higher CO₂ uptake found when the activation was carried out with carbon dioxide. Even at lower temperatures, the reaction rates of the carbon material with steam might be higher than with carbon dioxide, which would accelerate the development of the porosity.

According to the results from the RSM study, the temperature, heating rate and solid yield values selected for the activation in the vertical tube furnace were as follows: 885 °C, heating rate of 15 °C min⁻¹ and 12% of solid yield for the optimum CS activated with carbon dioxide; and 850 °C, heating rate of 15 °C min⁻¹ and 15.3% of solid yield for the CS activated with steam. These two optimum samples will be referred to as CS-CO₂ and CS-H₂O, respectively, hereafter.

3.2 Textural characterization of the optimum activated carbons

In Fig. 2, the N₂ and CO₂ adsorption isotherms at -196 and 0 °C, respectively, are plotted. Table 4 summarizes the textural parameters calculated from these isotherms. Both ACs are mainly microporous: the microporosity, as represented by W_{0,N2}, accounts for more than 83% of the total pore volume for CS-CO₂ and more than 70% in the case of CS-H₂O, which confirms the assumptions stated about the superior ability of carbon dioxide to create microporosity during the carbon material activation. It has been reported in the literature that carbon dioxide activation of almond shells and olive and peach stones mainly results in the creation of microporosity, whilst steam activation widens the microporosity from the early stages of the activation process, lowering the micropore volume in the resulting activated carbons.^{29,30} Likewise, according to the

shape of the N₂ adsorption isotherms (Fig. 2a), CS-CO₂ is nearly strictly microporous and displays a pronounced elbow at low relative pressures whereas CS-H₂O shows a linear increase in the N₂ uptake over the middle section of the isotherm and a characteristic hysteresis loop that denotes the presence of mesoporosity. The presence of mesoporosity could benefit the adsorption process dynamics as these pores could act as feeding pores. Average micropore widths around 0.9 nm and characteristic energies over 23 kJ mol⁻¹ were obtained for both cherry stones-based ACs (Table 4).

Regarding the assessment of the narrow microporosity (of less than 1 nm in size), the CO₂ adsorption isotherms of both ACs nearly overlapped up to relative pressures of 0.02 and slightly diverged from there, where the adsorbed volume was slightly higher for CS-CO₂ (Fig. 2b). Table 4 shows that similar features in terms of narrow micropores are encountered in both ACs, although slightly higher values of narrow micropore volume, W_{0,CO_2} , and narrow micropore surface, S_{mic,CO_2} , were obtained for CS-CO₂. The characteristic energy also addresses a slight difference between both ACs, pointing out a stronger interaction with CO₂ in the case of CS-H₂O. The average narrow micropore width, L_{0,CO_2} , for both adsorbents was between 0.7-0.8 nm. The micropore size distributions in the narrow microporosity range (Fig. 2c) reveal great similarities between both ACs. Nevertheless, the CO₂ activated carbon shows a broader distribution in the 0.5-0.7 nm range and the steam activated carbon presents a higher volume of micropores of approximately 0.5 nm.

It has been demonstrated that different porosity features (micro, meso and macroporosity) are developed during the activation of biomass precursors according to the activation conditions. This is in agreement with, previous works on biomass-derived adsorbents.^{4,5,7}

From the textural characterization of the cherry stones-based ACs it may be concluded that differences in the activation agent have an impact in the porosity development, although to a small extent, given that the preparation conditions were optimized in terms of a maximum CO₂ uptake at atmospheric pressure. The results showed that carbon dioxide activation promotes the development of microporosity whereas during steam activation micropores as well as mesopores are developed.

3.3 Adsorption and separation of CO₂/CH₄

The CO₂ uptakes obtained in the TGA at atmospheric pressure are higher than those of commercial activated carbons previously reported for CO₂ adsorption under similar conditions.³¹ Moreover, they are in good agreement or are higher than the CO₂ uptakes of biomass-based carbon adsorbents evaluated for post-combustion capture.^{27,28} Those results therefore show the potential of the produced activated carbons from cherry stones to be used as CO₂ adsorbents.

As a first step in the characterization of the two cherry stones-based ACs for CO₂/CH₄ separation purposes the pure component CO₂ and CH₄ adsorption isotherms were measured. Fig. 3a plots the experimental CO₂ and CH₄ adsorption isotherms at 30 °C on both cherry stones-based ACs. The isotherms are Type I in IUPAC classification. Both CS activated carbons showed preferential adsorption of CO₂ over CH₄ in the pressure range tested. The microporosity in both samples seems large enough to neglect shape selectivity effects based on the kinetic diameters of the two gas molecules (3.30 Å for CO₂ and 3.80 Å for CH₄)³². However, the large quadrupolar moment of CO₂ (CH₄ does not hold a quadrupole moment) may account for such a difference in adsorption performance. The quadrupole moment produces a strong attraction to the adsorbent surface that results in an increased uptake. The polarizability

could also influence the adsorption performance. Nevertheless, both CO₂ and CH₄ show high polarizability ($31 \times 10^{-25} \text{ cm}^3$ for CO₂ and $26 \times 10^{-25} \text{ cm}^3$ for CH₄)³² and this attraction force is much weaker than the quadrupole moment.

The performance of both materials to CO₂ and CH₄ adsorption presents great similarities: the isotherms nearly overlapped at subatmospheric pressures but CS-CO₂ attains greater uptakes in the higher pressure range.

The fittings of the pure component CO₂ and CH₄ adsorption data at 30 °C to the Sips model (Eq. (6)) are also plotted (lines) in Fig. 3a. The optimal parameters and squared relative errors from the performed fittings are listed in Table 5. Fig. 3a shows that the Sips model fitted with good accuracy the experimental CO₂ and CH₄ adsorption data over the tested pressure range. However, small deviations of the model from the experimental CH₄ adsorption data occur in the pressure range above 5 bar. It has to be borne in mind that during the optimization procedure, the saturation loading and the parameter n (heterogeneity) for both adsorbates, CO₂ and CH₄, were considered equal. This may impact to a greater extent the adsorbate with the weaker affinity, i.e., CH₄. The goodness of the fitting is corroborated by the small values of the *SRE* reported in Table 5. The affinity constants for CO₂ (b_{CO_2}) are one order of magnitude greater than those for CH₄ (b_{CH_4}). The stronger affinity towards CO₂ is clearly reflected in the greater experimental CO₂ uptakes from the adsorption isotherms and may account for this difference. The values of the parameter n show certain heterogeneity in the system that would not be adequately represented by the more conventional and theoretical Langmuir equation.

Table 5 shows that the fitting of the adsorption data to the Sips model for both cherry stones-based ACs delivers similar values of the optimized parameters.

Nevertheless, a small difference is seen in the value of the saturation loading, q_s , which is higher in the case of the CS-CO₂ activated carbon. The fitted values of the saturation loading, q_s , of both adsorbents are in good agreement with those found in the literature for commercial activated carbons.³³

Based on the fitted parameters from the pure component adsorption data, the multicomponent Sips equation (Eq. (8)) was used to predict the adsorption performance of CO₂ and CH₄ in binary mixtures at 30 °C and 3 bar. These conditions were selected to be representative of CO₂ separation from biogas streams. Fig. 3b shows the predicted isotherms for both cherry stones-based activated carbons. The selectivity of both ACs to separate CO₂ from CO₂/CH₄ binary mixtures was estimated from the following expression:

$$S_{CO_2/CH_4} = \frac{q_{CO_2}/q_{CH_4}}{y_{CO_2}/y_{CH_4}} \quad (11)$$

where q_{CO_2} and q_{CH_4} were estimated from the multicomponent Sips model for the different molar fractions of CO₂ (y_{CO_2}) and CH₄ (y_{CH_4}) in the binary mixtures.

The pure component CO₂ and CH₄ uptakes at 3 bar for both cherry stones-based ACs are represented by the predicted multicomponent uptakes at CH₄ mole fractions of 0 and 1, respectively. As expected, both components show a decreasing trend in the uptake with increasing mole fraction of the other component in the binary mixture. On the other hand, the adsorption of CH₄ from a binary mixture seems to be more affected than that of CO₂: CH₄ only holds a 27% of the pure component uptake when mixed with CO₂ in a 50:50 binary mixture whereas CO₂ keeps a 65% of the pure component adsorption capacity at 3 bar. On the other hand, the performance of both cherry stones-based ACs is very similar in terms of the predicted CO₂ and CH₄ uptakes from binary mixtures at 3 bar in agreement with the pure component experimental adsorption data at

this pressure. Moreover, both carbons show a decreasing trend in the selectivity to separate CO₂ with increasing CH₄ mole fraction. At 3 bar the selectivity of the cherry stones-based ACs for CO₂ remains in the range of 3.2-4, which is higher than the values reported from experimental data of mesocarbon microbeads³⁴ and activated carbon beads³⁵ as well as from molecular simulations in slit shaped pores.³⁶ On the other hand, the values of the selectivity for both carbons differ and CS-H₂O shows enhanced selectivity to separate CO₂ from CO₂/CH₄ binary mixtures at 3 bar than CS-CO₂. The narrower character of the microporosity in CS-H₂O could account for such a difference.

4 CONCLUSIONS

Two low cost carbon adsorbents, CS-CO₂ and CS-H₂O, were produced from cherry stones by single-step activation with CO₂ and steam, respectively. The effect of activation temperature, heating rate and solid yield on the CO₂ uptake of the biomass-based activated carbons was evaluated by means of the Response Surface Methodology. The most influential variable on the CO₂ uptake was the activation temperature for the CS-CO₂ adsorbent and the solid yield for the CS-H₂O activated carbon.

The highest CO₂ uptakes achieved at 25 °C and atmospheric pressure were: 11.45 wt.% when the precursor was activated with carbon dioxide and 10.56% when the precursor was activated with steam. Carbon dioxide activation promoted the development of microporosity whereas during steam activation both micropores and mesopores were developed. Pure and multicomponent adsorption tests at 3 bar on the optimum activated carbons showed a similar CO₂/CH₄ separation performance for CS-CO₂ and CS-H₂O. Even though the adsorbent activated with carbon dioxide showed a slightly higher adsorption capacity, the activation with steam led to a slightly more selective activated carbon to separate CO₂ from CH₄. In summary, due to their textural

development and low cost, the cherry stones-based activated carbons prepared are deemed as good adsorbents in CO₂ adsorption based applications; more precisely for the separation of CO₂ from CO₂/CH₄ mixtures.

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Figure captions

Fig. 1. Response surface and contour plots for the CO₂ capture capacity as a function of the activation temperature and solid yield corresponding to the carbon dioxide activated-CS (a) and steam activated-CS (b) adsorbents.

Fig. 2. N₂ adsorption isotherms at -196 °C (a), CO₂ adsorption isotherms at 0 °C (b) and micropore size distributions assessed from the NLDFT-CO₂ slit shaped carbon model (c) for the optimum cherry stones-based activated carbons.

Fig. 3. CO₂ and CH₄ adsorption isotherms at 30 °C (a) and predicted CO₂ and CH₄ adsorption and selectivity for binary CO₂/CH₄ mixtures at 3 bar and 30 °C (b) for the cherry stones-based activated carbons.

Table 1 Proximate and ultimate analyses of the raw cherry stones (CS) used as carbon precursor in the present work

Sample	CS
Proximate analysis ^a	
Moisture (wt.%)	3.90
Volatile matter (wt.%, db)	82.78
Ash (wt.%, db)	0.40
Fixed carbon (wt.%, db) ^b	16.82
Ultimate analysis (wt.%, daf) ^a	
C	52.76
H	6.18
N	0.76
S	0.02
O ^b	40.28

db: dry basis; daf: dry and ash free bases.

^a The proximate analysis was conducted in a LECO TGA-601, and the ultimate analysis in a LECO CHNS-932.

^b Calculated by difference.

Table 2 Independent variables and experimental values of the response variable for the central composite design (CCD) using the CS adsorbents

Run	Independent variables			Response
	<i>T</i> (°C)	<i>HR</i> (°C min ⁻¹)	<i>Y</i> (%)	CO ₂ capture (%)
<i>Carbon dioxide activated-CS</i>				
1	790.5 (-1)	12.03 (-1)	9.03 (-1)	10.57
2	909.5 (+1)	12.03 (-1)	9.03 (-1)	11.52
3	790.5 (-1)	17.97 (+1)	9.03 (-1)	10.61
4	909.5 (+1)	17.97 (+1)	9.03 (-1)	10.97
5	790.5 (-1)	12.03 (-1)	14.97 (+1)	10.54
6	909.5 (+1)	12.03 (-1)	14.97 (+1)	10.95
7	790.5 (-1)	17.97 (+1)	14.97 (+1)	10.44
8	909.5 (+1)	17.97 (+1)	14.97 (+1)	10.97
9 ^a	850.0 (0)	15.00 (0)	12.00 (0)	11.24
10	750.0 (-1.682)	15.00 (0)	12.00 (0)	9.60
11	950.0 (+1.682)	15.00 (0)	12.00 (0)	11.22
12	850.0 (0)	10.00 (-1.682)	12.00 (0)	11.89
13	850.0 (0)	20.00 (+1.682)	12.00 (0)	11.35
14	850.0 (0)	15.00 (0)	7.00 (-1.682)	10.03
15	850.0 (0)	15.00 (0)	17.00 (+1.682)	10.99
<i>Steam activated-CS</i>				
1	790.5 (-1)	12.03 (-1)	10.04 (-1)	9.64
2	909.5 (+1)	12.03 (-1)	10.04 (-1)	9.72
3	790.5 (-1)	17.97 (+1)	10.04 (-1)	9.56
4	909.5 (+1)	17.97 (+1)	10.04 (-1)	9.58
5	790.5 (-1)	12.03 (-1)	18.96 (+1)	10.10
6	909.5 (+1)	12.03 (-1)	18.96 (+1)	10.15
7	790.5 (-1)	17.97 (+1)	18.96 (+1)	9.83
8	909.5 (+1)	17.97 (+1)	18.96 (+1)	10.54
9 ^a	850.0 (0)	15.00 (0)	14.50 (0)	10.50
10	750.0 (-1.682)	15.00 (0)	14.50 (0)	9.95
11	950.0 (+1.682)	15.00 (0)	14.50 (0)	10.13
12	850.0 (0)	10.00 (-1.682)	14.50 (0)	10.44
13	850.0 (0)	20.00 (+1.682)	14.50 (0)	10.66
14	850.0 (0)	15.00 (0)	7.00 (-1.682)	8.42
15	850.0 (0)	15.00 (0)	22.00 (+1.682)	8.90

^a Central point mean of six replicates

T: activation temperature; *HR*: heating rate; *Y*: solid yield.

Table 3 Results of multiple regression analysis and ANOVA for the fit of the polynomial model to the CO₂ capture capacity experimental data of activated carbons

	Carbon dioxide activated-CS				Steam activated-CS			
	Coded coefficient	Sum of squares	DF	<i>p</i> -value	Coded coefficient	Sum of squares	DF	<i>p</i> -value
Intersection	11.235	758.836	1	0.000	10.494	662.037	1	0.000
<i>T</i>	0.364	1.812	1	0.002	0.085	0.099	1	0.125
<i>HR</i>	-0.110	0.164	1	0.229	0.020	0.627	1	0.704
<i>Y</i>	0.062	0.052	1	0.485	0.214	0.005	1	0.002
<i>T</i> ²	-0.292	1.229	1	0.006	-0.124	0.220	1	0.033
<i>HR</i> ²	0.136	0.265	1	0.135	0.057	5.387	1	0.276
<i>Y</i> ²	-0.257	0.950	1	0.013	-0.611	0.046	1	0.000
<i>T</i> · <i>HR</i>	-0.059	0.028	1	0.609	0.075	0.054	1	0.283
<i>T</i> · <i>Y</i>	-0.046	0.017	1	0.687	0.083	0.045	1	0.241
<i>HR</i> · <i>Y</i>	0.054	0.023	1	0.640	0.043	0.014	1	0.534
<i>T</i> · <i>HR</i> · <i>Y</i>	0.089	0.063	1	0.445	0.090	0.065	1	0.204
Model		4.647	10	0.014		6.578	10	0.000
Residual		0.887	9			0.311	9	
Total		5.535	19			6.889	19	
Lack-of-fit		0.641	4	0.114		0.189	4	0.243
Pure error		0.247	5			0.122	5	
<i>R</i> ²	0.840				0.955			
Adj- <i>R</i> ²	0.662				0.905			
AAD (%)	2.07				1.31			

Table 4 Textural characteristics of the optimum cherry stones-based activated carbons

Sample	N ₂ adsorption at -196 °C						CO ₂ adsorption at 0 °C			
	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	W _{0,N2} (cm ³ g ⁻¹)	L _{0,N2} (nm)	E _{0,N2} (kJ mol ⁻¹)	S _{mic,N2} (m ² g ⁻¹)	W _{0,CO2} (cm ³ g ⁻¹)	L _{0,CO2} (nm)	E _{0,CO2} (kJ mol ⁻¹)	S _{mic,CO2} (m ² g ⁻¹)
CS-CO ₂	1045	0.48	0.40	0.93	23.0	848	0.35	0.78	25.3	906
CS-H ₂ O	998	0.53	0.38	0.89	23.6	847	0.33	0.74	26.0	899

Table 5 Optimal parameters calculated from the fitting of the pure component CO₂ and CH₄ adsorption isotherms at 30 °C to the Sips model

Sample	q_s (mmol g ⁻¹)	n	b_{CO_2}	b_{CH_4}	SRE (%)
CS-CO ₂	10.45	1.40	1.7×10^{-3}	4.7×10^{-4}	3.27
CS-H ₂ O	9.31	1.39	2.1×10^{-3}	5.2×10^{-4}	2.42

Fig. 1 Response surface and contour plots for the CO₂ capture capacity as a function of the activation temperature and solid yield corresponding to the carbon dioxide activated-CS (a) and steam activated-CS (b) adsorbents.

Fig. 2 N₂ adsorption isotherms at -196 °C (a), CO₂ adsorption isotherms at 0 °C (b) and micropore size distributions assessed from the NLDFT-CO₂ slit-shaped carbon model (c) of the optimum cherry stones-based activated carbons.

Fig. 3 CO₂ and CH₄ adsorption isotherms at 30 °C (a) and predicted CO₂ and CH₄ adsorption and selectivity for binary CO₂/CH₄ mixtures at 3 bar and 30 °C (b) for the cherry stones-based activated carbons.