Breakthrough adsorption study of a commercial activated carbon for pre-combustion CO₂ capture

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Abstract

In this study a commercial activated carbon (Norit R2030CO₂) was assessed as a solid sorbent for precombustion CO₂ capture. This technology involves the removal of CO₂ from the shifted-syngas prior to the generation of electricity and the production of high-purity clean H₂. The CO₂ equilibrium adsorption capacity and breakthrough time were evaluated in a flow-through system where the adsorbent was subjected to four consecutive adsorption-desorption cycles. A CO₂/H₂/N₂ gas mixture (20/70/10 vol.% at normal conditions) was employed as the influent gas stream. Response surface methodology (RSM) was used to assess the combined effect of the adsorption CO₂ partial pressure and temperature (independent variables) on CO₂ capture capacity and breakthrough time (response variables) for the activated carbon. The CO₂ partial pressure ranged from 1 to 3 bar within a total pressure range of 5 to 15 bar and a temperature range of 25 to 65 °C. No interaction effect between the two independent variables on the responses was found. The CO₂ partial pressure was observed to be the most influential variable, with high values leading to an increase in both the CO₂ capture capacity and the breakthrough time. However, an increase in the temperature led to a decrease in both response variables. The maximum values of the response variables within the experimental region studied were obtained at 25 °C and under a CO₂ partial pressure of 3 bar (15 bar total pressure).

Keywords: Pre-combustion; Activated carbon; CO₂ capture; Breakthrough time; Response surface methodology

1. Introduction

Massive reductions in CO₂ emissions need to be achieved if permanent damage to the environment is to be avoided. Carbon capture and storage (CCS) is a group of technologies that have the potential to reduce, in the near term, emissions from large fixed industrial sources into the atmosphere. CO₂ capture is the most costly component of the CCS process (between half and two thirds of the total cost of CCS). This has

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prompted substantial research on how to reduce the cost, while achieving significant levels, of CO₂ capture.

For existing power plants, CO₂ needs to be removed from a diluted (< 15% by volume) flue gas stream, i.e., post-combustion capture. Alternative power plant designs include integrated gasification combined cycle (IGCC) plants, where the CO₂ can be selectively separated from the shifted-syngas (CO₂/H₂) prior to the generation of electricity, i.e., pre-combustion capture. In this case the gas stream is under pressure and contains a high concentration of CO₂. The most developed pre-combustion CO₂ capture option for coal-fired power generation is the use of physical solvents, such as SelexolTM or Rectisol® [1]. However, these two processes are expensive and entail a significant amount of utility consumption. As an alternative to physical solvents, adsorption using solid sorbents is a promising technology that offers potential energy savings with lower capital and operating costs [2-4]. Solid sorbents can interact with the adsorbate via strong chemisorption interactions or by weak physical adsorption. For applications where CO₂ is at a high pressure, i.e., gasification (pre-combustion capture), physical adsorbents are sufficiently effective. However, for CO₂ adsorption at low pressure (post-combustion capture), adsorbents with strong basic functionalities are required.

A wide variety of solid sorbents is currently under study to separate CO₂ from energy-generating coal-fired power plants such as zeolites, activated carbons, calcium oxides, hydrotalcites, supported amines and metal-organic framework (MOF) materials [3, 5-10]. Physisorbents such as activated carbons (AC) and aluminosilicate zeolite molecular sieves show considerable promise for CO₂ adsorption because of their good adsorption capacities, rapid adsorption kinetics and low regeneration energies. In general, the CO₂ adsorption capacities of AC are lower than those of zeolites under low pressure. However, at higher pressures, the CO₂ uptake of AC can surpass that of zeolites [3, 11]. Additionally, AC have a hydrophobic character [6] and can be produced from a wide variety of sources (coal, industrial byproducts, biomass sources, etc.), which makes them cheaper to produce on an industrial scale than other sorbents. Several studies have been published on the potential application of AC to post-combustion [12-18] and pre-combustion [19-22] capture processes.

The adsorption capacity of activated carbons has been examined by several authors but on an equilibrium basis only. However, the dynamic regime of operation is equally

important as a material characteristic, since most applications of adsorption are run only to partial bed saturation because of adsorption dynamics. Solid adsorbents are typically employed in cyclic, multimodule processes of adsorption and desorption, with desorption being induced by a swing in pressure or temperature. Hence, analyses using a dynamic test rig are required to ascertain the extent to which the equilibrium uptake may be translated into breakthrough capacity.

Response surface methodology (RSM) is a multivariable statistical technique used to optimize all kinds of processes, i.e., to elucidate the conditions at which to apply a procedure in order to obtain the best possible response in the experimental region studied. This methodology involves the design of experiments and multiple regression analysis as tools to assess the effects of two or more independent variables on dependent variables [23]. One additional advantage is the possibility of evaluating the interaction effect between the independent variables on the response. This technique is based on the fit of a polynomial equation to the experimental data, to describe the behaviour of a given set of data. Thus, a mathematical model which describes the studied process is generated. The objective of this technique is to simultaneously optimize the levels of the studied variables in order to attain the best process performance [24]. Only recently have studies been published on the application of RSM in matters related to CO₂ adsorption. Thus, Serna-Guerrero et al. [25] studied the optimum regeneration conditions (temperature, pressure and flow rate of purge gas) of an amine-bearing adsorbent for CO₂ removal, while Mulgundmath and Tezel [26] studied the optimization of carbon dioxide recovery from flue gas in a TPSA system in relation to the purge/feed flow ratio, purge time, purge gas temperature and adsorption pressure.

In this work, the CO₂ capture capacity and the breakthrough time of a CO₂/H₂/N₂ gas mixture of constant composition (20/70/10 vol.% at normal conditions) were studied by means of response surface methodology using an activated carbon in a fixed-bed reactor. The objectives of this study were: (i) to assess the combined effect of CO₂ partial pressure and temperature on CO₂ capture capacity and breakthrough time, and (ii) to determine the optimum values that maximize both the CO₂ capture capacity and the breakthrough time within the experimental region under study.

2. Materials and methods

2.1. Materials

A commercial activated carbon supplied by Norit (Norit R2030 CO₂) was chosen as a reference case for use as a means of comparing newly developed, tailored adsorbents. The activated carbon is a steam activated peat-based extruded carbon with a diameter of 3 mm. A fully detailed chemical and textural characterisation of this carbon has been reported previously [27].

2.2. *Dynamic column breakthrough measurements – Experimental apparatus and procedure*

The CO₂ equilibrium (i.e., saturation) adsorption capacities of the activated carbon and dynamic column breakthrough measurements for the CO₂-containing ternary gas mixture were conducted in a purpose-built fixed-bed adsorption unit (Figure 1). The stainless steel fixed-bed reactor was 203 mm in height, 9 mm in diameter and was equipped with a porous plate located 46 mm from the base of the column. The gas manifold system consisted of three lines fitted with mass flow controllers from Bronkhorst High-Tech with flows ranging between 1 and 200 NmL/min. The controllers have an accuracy of 1% full scale and a repeatability of 0.1% full scale. One of the lines is used to feed in an inert gas, N₂, in order to dry the sample before each experiment. The other two lines feed in CO₂ and H₂ so that different gas mixtures akin to the concentrations representative of different pre-combustion capture gas streams can be prepared. The gases flowing through the different lines are mixed in a helicoidal distributor that ensures perfect mixing of the feed gas before it enters the bed.

A K-type thermocouple, located at a height of 45 mm above the porous plate (exit end of the column), was used to continuously monitor the column temperature with an accuracy of ± 1.5 °C. The temperature was controlled by coupling the heating element coiled around the reactor to an air-cooling device. The bed pressure was controlled by means of a back-pressure regulator located in the outlet pipe with a repeatability of 0.5% full scale (0-40 bar). The system was also equipped with a continuous gas analyzer, a dual channel micro-gas chromatograph (micro-GC), CP 4900 from Varian, fitted with a thermal conductive detector (TCD) in which He and Ar are used as the

carrier gases. The TCD response was calibrated employing CO₂/H₂/N₂ mixtures of known composition.

The bed was packed with activated carbon in order to measure the dynamics of the CO₂ in the column. The physical properties of the adsorbent along with the characteristics of the bed are summarized in Table 1.

In a representative cyclic adsorption-desorption experiment (Figure 2), the sorbent is dried (i.e., cleaned) by flowing N₂ (50 NmL/min) for 50 min at 100°C and atmospheric pressure. After the drying step, the bed temperature and pressure are raised to the adsorption values in a pre-conditioning step of 10 min, where 50 NmL/min of N₂ are allowed to flow through the system. This is followed by the adsorption step in which a CO₂/H₂/N₂ gas mixture (20/70/10% v/v) is fed through the pre-cleaned and pre-conditioned column (filled with N₂ at the adsorption temperature and pressure) for 60 min. The feed gas inlet flowrate was kept constant (100 NmL/min). Three different adsorption pressures were tested (5, 10 and 15 bar), corresponding to CO₂ partial pressures of 1, 2 and 3 bar, respectively, at three different adsorption temperatures (25, 45 and 65 °C). The CO₂ composition in the column effluent gas was continuously monitored as a function of time (breakthrough curve) until the composition approached the inlet gas composition value, i.e., until saturation was reached. The adsorbed CO₂ was completely desorbed by switching the gas flowrate to 5 NmL/min of N₂, lowering the pressure to atmospheric and raising the temperature to 80 °C for 60 min. The sorbent was subjected to four consecutive adsorption-desorption cycles and its maximum CO₂ adsorption capacity at different pressures and temperatures as well as breakthrough times were assessed.

The specific equilibrium amount of adsorbed CO₂ for a specific temperature and CO₂ partial pressure can be determined by applying the following mass balance equation to the bed:

$$q_{CO_2} = \frac{1}{m_{adsorbent}} \left[\int_0^{t_b} (F_{CO_{2,in}} - F_{CO_{2,out}}) dt - \frac{y_{CO_{2,feed}} P_b R T_b V_b}{Z R T_b} - \frac{y_{CO_{2,feed}} P_b V_d}{Z R T_b} \right] \quad [1]$$

where q_{CO_2} stands for the specific CO₂ adsorption capacity of the adsorbent, $m_{adsorbent}$ is the mass of adsorbent in the bed, $F_{CO_{2,in}}$ and $F_{CO_{2,out}}$ refer to the molar flowrate of

CO₂ at the inlet and outlet of the bed, respectively, t_s refers to the time required to reach saturation, $y_{CO_2, feed}$ is the molar fraction of CO₂ in the feed stream, P_b and T_b are the pressure and temperature of bed at equilibrium, ε_T is the total porosity of the bed, V_b is the bed volume, V_d is the dead volume in the bed, Z is the CO₂ compressibility factor at P_b and T_b , and R is the universal gas constant. In our case, t_s was the time at which the bed is completely saturated, which means that the CO₂ concentration at the bed outlet equals the feed concentration, $y_{CO_2, out} = y_{CO_2, feed}$. The total porosity of the bed is calculated by means of the following equation [28]:

$$\varepsilon_T = \varepsilon_b + (1 - \varepsilon_b) \varepsilon_p \quad [2]$$

where ε_b is the packed bed porosity and ε_p is the particle porosity. In equation [1] the term (A) is the total number of moles of CO₂ retained by the column over the cycle time and can be calculated by a graphical method that makes use of the outlet CO₂ concentration and the feed flowrate. This methodology avoids the need to know the variation of the molar CO₂ flowrate at the bed exit; it simply calculates the total mass retained by the column as a percentage (ratio of the adsorbed area to the total area on a graph of CO₂ concentration, % v/v, versus time, min) of the total mass that entered the system [29]. Terms (B) and (C) are correction factors to account for the CO₂ gas which has accumulated in the intraparticle voids and dead space of the bed, respectively.

2.3. Response Surface Methodology

Independent variables or factors are experimental variables that can be changed independently of each other. In this work, they were the CO₂ partial pressure (P_{CO_2}) and the temperature (T). The levels of these variables are the different values at which the experiments must be carried out. In this study, both independent variables were investigated at three levels. Thus, P_{CO_2} was studied at 1, 2 and 3 bar; whereas T was studied at 25, 45 and 65 °C. The responses or dependent variables are those which are measured during the experiments. In this work, the response variables were the CO₂ capture capacity and the breakthrough time (t_b).

Before applying RSM methodology, it is necessary to choose an experimental design that will define which experiments should be carried out in the experimental region

under study. The design will define a set of different combinations for the levels of the independent variables that must be applied experimentally to obtain the responses. In this work a three-level full factorial design was chosen. It involved 13 experiments, which are shown in Table 2, including nine factorial points and four additional replicates at the centre of the design. These replicates made it possible to estimate the experimental error associated with the repetitions. All the experiments were conducted in a random order.

The mathematical-statistical treatment of experimental data consists in fitting a polynomial function to a set of data. In this work, which employed two independent variables, x_1 and x_2 , the following second-order polynomial equation was applied:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \varepsilon \quad [3]$$

where β_0 is the constant term, β_1 and β_2 represent the coefficients of the linear parameters, β_{12} represents the coefficient of the interaction parameter, β_{11} and β_{22} represent the coefficients of the quadratic parameters and ε is the residual associated with the experiments. Multiple regression analysis was used to fit Eq. [3] to the experimental data by means of the method of least squares, which makes it possible to determine the β coefficients that generate the lowest possible residual. The equation obtained describes the behaviour of the response in the experimental region as a function of the independent variables. An evaluation of the fitness of the model was carried out by applying an analysis of variance (ANOVA) and lack-of-fit test. A model fits the experimental data well if it presents a significant regression and a non-significant lack of fit. To establish whether a parameter is significant, a p -value test to a 95% level of confidence was applied to the experimental results. The coefficient of determination adjusted by taking into account the number of variables ($\text{Adj-}R^2$) and the absolute average deviation (AAD) were calculated in order to check the accuracy of the model. $\text{Adj-}R^2$ must be close to 1.0 and the AAD between the predicted and observed data has to be as small as possible. $\text{Adj-}R^2$ represents the proportion of variability of the data that is accounted for by the model. The ADD is a direct parameter that describes the deviations between the experimental and calculated values and it is calculated by means of the following equation [30]:

$$\text{AAD (\%)} = 100 \times [\sum_{i=1}^n (|y_{i,\text{exp}} - y_{i,\text{cal}}|/y_{i,\text{exp}})]/n \quad [4]$$

where $y_{i,\text{exp}}$ and $y_{i,\text{cal}}$ are the experimental and calculated responses, respectively, and n is the number of experiments. The statistical analyses were carried out using SPSS Statistics 17.0 software.

The model obtained can be three-dimensionally represented as a surface (response surface plot) and the best operation conditions inside the experimental region studied can be found by visual inspection. The two-dimensional display of the surface plot generates the contour plot, in which the lines of constant response are drawn on the plane of the independent variables. Response surface and contour plots were generated using SigmaPlot 8.0 software. After this, the optimum values for each independent variable that would produce the best response in the experimental region under study were obtained.

3. Results and discussion

3.1. Column breakthrough adsorption experiments

Breakthrough adsorption experiments for activated carbon NoritR2030 were carried out at different adsorption temperatures and pressures, where the feed gas containing a constant CO₂ concentration was passed over the “fresh” adsorbent. The progress of the effluent concentration from the bed when subjected to a concentration input variation was recorded, i.e., its breakthrough curve. Two parameters were calculated to estimate the CO₂ column dynamics: the equilibrium CO₂ adsorption capacity and the breakthrough time, t_b , or break point, which is the time it takes for CO₂ to be detected at the adsorption column outlet. In a typical operation, the flow would be stopped or diverted to a fresh adsorbent bed once the CO₂ concentration reached this limit [31, 32]. However, in this case, experiments were conducted until saturation was reached, i.e., until the point at which the outlet CO₂ concentration equals that of the inlet stream, in order to assess the maximum dynamic adsorption capacity of the adsorbent. During the desorption step the adsorbent was fully regenerated so that the repeatability of the breakthrough curves could be assessed.

An example of a complete breakthrough adsorption experiment is depicted in Figure 3, where the bed pressure, temperature and gas outlet concentrations can be followed. The overall pattern of the dynamic behavior of an adsorption column, i.e., the shape of the breakthrough curve or concentration front, is generally determined by the adsorption equilibrium [32] and may be distended due to both hydrodynamic (axial dispersion) and kinetic (finite resistance to mass transfer) effects [33].

The breakthrough curves were measured for the activated carbon and C/C_0 (concentration of CO_2 in the fluid relative to that of the CO_2 in the feed) was plotted versus time (Figure 4). At first, most of the mass transfer takes place near the bed inlet where the fluid first makes contact with the adsorbent. With time and once the solid near the inlet becomes saturated, the mass-transfer zone (which is S-shaped), where most of the change in concentration occurs, moves down the bed farther away from the inlet. At the break point, the solid between the bed inlet and the start of the mass-transfer zone is completely saturated (at equilibrium with the feed). In the ideal case of no mass-transfer resistance and no axial dispersion, the mass-transfer zone would be of infinitesimal width, and the breakthrough curve would be a vertical line from 0 to 1.0 when all the solid is saturated [31].

Adsorption temperature and pressure affect the shape of the breakthrough curve as well as the breakthrough time (Figure 4). At a given adsorption temperature and CO_2 concentration in the feed (Figure 4a, b and c) a higher adsorption pressure (i.e., a higher CO_2 partial pressure) leads to longer breakthrough times because the CO_2 concentration front takes more time to reach the bed outlet. For example, at 25 °C (Figure 4a) the CO_2 adsorption front reaches the bed outlet after 5 min at 5 bar ($P_{\text{CO}_2}=1$ bar) and this time increases to 10.5 min at 15 bar ($P_{\text{CO}_2}=3$ bar). Conversely, at a given adsorption pressure and CO_2 concentration in the feed (Figure 4d, e and f), a higher adsorption temperature results in shorter breakthrough times. For instance, at 5 bar (Figure 4d) the breakthrough time is 5.62, 3.85 and 3.18 min for 25, 45 and 65 °C, respectively. Thus, the breakthrough times are proportional to the total pressure in the system and to the reciprocal of the adsorption temperature. The repeatability of the breakthrough experiments can also be appreciated in Figure 4 for each series of tests (identified by the same colour) since the breakthrough curves overlap perfectly.

A narrow mass-transfer zone is desirable to make efficient use of the adsorbent and to reduce the energy costs of regeneration. The narrower the mass-transfer zone, the greater the degree of utilization of the bed: if the mass-transfer zone is narrow relative to the bed length, the breakthrough curve will be rather steep and most of the solid capacity will be utilized at the breakpoint. However, when the mass-transfer zone is almost as long as the bed, the breakthrough curve is more distended and less than half of the bed's capacity is utilized [31]. Breakthrough curves at a given temperature (Figures 4a, b and c) show that, as the pressure increases, the mass-transfer zone becomes broader, i.e., mass transfer is slower because of axial dispersion. On the other hand, a temperature increase at a given pressure (Figures 4d, e and f) favours mass transfer and, consequently, the concentration profile becomes steeper and the mass-transfer zone becomes narrower.

Column inefficiency, due to mass transfer resistance during the adsorption, was estimated from the percentage of unused bed, which can be converted to an equivalent length of unused bed (LUB) [34]. To calculate the percentage of unused bed from the breakthrough curve, the total solute adsorbed up to the break point was determined by integration. The capacity of the solid was obtained by integrating the complete breakthrough curve. The ratio of these two quantities is the fraction of the bed capacity utilized at the break point and 1.0 minus this ratio is the unused fraction. At a given temperature (Figure 5) an increase in pressure makes the column more inefficient, i.e., the percentage of unused bed is higher, which is in good agreement with the distended breakthrough curves observed at higher pressures (Figure 4a, b and c). Higher pressures also affect the column inefficiency more than lower ones: for instance, at 25 °C the percentage of unused bed at 1 and 2 bar rises from 29.9 to 30.5% respectively, whereas it increases to 33.7% at 3 bar. Conversely, at a certain pressure, increasing temperatures favour the column efficiency due to the enhanced effect on mass transfer rates, i.e., kinetics. For instance, at a CO₂ partial pressure of 1 bar the percentage of unused bed drops from 29.9 to 16.3% when the adsorption temperature increases from 25 to 65 °C. Again, this observation is in good agreement with the steeper breakthrough curves obtained in Figures 1d, e and f at higher temperatures.

The equilibrium dynamic capacity is determined from the breakthrough curve. Values obtained from the breakthrough experiments (Table 2) indicate that, as would be

expected in a physical adsorption process, the adsorption capacity of Norit R2030, like those of other physisorbents such as zeolites, decreases rapidly as the temperature increases. This is because adsorption is an exothermic process and it is favoured at lower temperatures. Conversely, the adsorption capacity increases with increasing pressure. For instance, the capacity values obtained at 10 bar and three different temperatures (25, 45 and 65 °C) dropped from 3.02 to 2.04 mol CO₂/kg adsorbent as the temperature increased from 25 to 65 °C; however, the adsorption capacities at 45 °C and three different pressures (5, 10 and 15 bar) rose from 1.70 to 3.32 mol CO₂/kg adsorbent as the pressure increased from 5 to 15 bar (Table 2). The break-point time is proportional to the capacity of the solid in all the cases studied (Table 2) so we can conclude that for a given temperature or pressure, the highest adsorption capacity corresponds to the longest breakthrough time.

3.2. Evaluation of CO₂ capture dynamics by means of response surface methodology

In order to apply the RSM, the levels of the independent variables, i.e., adsorption temperature and CO₂ partial pressure, must be coded in order to be able to compare variables with different units or of different orders of magnitude, so that they will all affect the response evenly, making the units of the parameters irrelevant. Codification of the levels of the variables consists in transforming each real value into coordinates inside a scale with dimensionless values, which must be proportional to their location in the experimental space. In Table 2, the coded values of the independent variables are shown in parentheses. The experimental values obtained for the response variables are also presented in Table 2.

Table 3 shows the results of the fit of Eq. [3] to the experimental data by multiple regression analysis and those of the evaluation of the fitness of the model by ANOVA, together with the Adj- R^2 and AAD values. The coefficient values of the polynomial models presented in Table 3 are coded coefficients, since the values of the independent variables were also coded. A comparison of these values indicates that the CO₂ partial pressure was the most influential variable on both the CO₂ capture capacity and the breakthrough time during the capture process.

The ANOVA tests showed which of the terms of the models were statistically significant to a 95% confidence level (p -value<0.05), and those that were not

statistically significant ($p\text{-value}>0.05$) were eliminated from the models. It can also be observed that the models obtained for both response variables were statistically significant to a 95% confidence level ($p\text{-value}<0.05$), whereas their lack of fit was found to be statistically non-significant to a 95% confidence level ($p\text{-value}>0.05$). On the other hand, the $\text{Adj-}R^2$ and the AAD values were acceptable: 0.969 and 3.4%, respectively, for CO_2 capture capacity; and 0.984 and 2.0, respectively, for breakthrough time.

No interaction effect between the two independent variables, adsorption CO_2 partial pressure and temperature, was found, since the interaction term in the model, x_1x_2 , proved to be statistically non-significant to a 95% confidence level ($p\text{-value}>0.05$). Once the non-significant terms were eliminated, the coded coefficient values were decoded in order to obtain the polynomial models for the response variables as a function of the actual independent variables. The models obtained were the following:

$$\text{Capture capacity (mol CO}_2\text{/kg adsorbent)} = 3.1210 - 0.0779 T + 0.8067 P_{\text{CO}_2} + 0.0006 T^2 \quad [5]$$

$$\text{Breakthrough time, } t_b, \text{ (min)} = 8.0421 - 0.2394 T + 2.4067 P_{\text{CO}_2} + 0.0020 T^2 \quad [6]$$

The regression equations for CO_2 capture capacity and breakthrough time show that both depend directly on the P_{CO_2} and inversely on the T and the square of T . Figure 6 represents the response surface plots and the contour plots for the CO_2 capture capacity and for the breakthrough time, t_b , as a function of the independent variables, P_{CO_2} and T . It can be observed that the CO_2 capture capacity and the breakthrough time increase as P_{CO_2} increases and T decreases. In addition, there is a curvature in the response surface and the contour plot isolines, which indicates that the effect of the temperature on the response variables varies over the experimental range studied. Thus, when CO_2 adsorption is carried out at high temperatures, a greater temperature decrease is necessary to obtain the same increase in the responses as that achieved at lower temperatures, indicating that, as the temperature increased, its effect on the responses diminished. Figure 6 also shows that, when the CO_2 adsorption was carried out at 25 °C and 3 bar CO_2 partial pressure, the maximum values of CO_2 capture capacity (3.96 mol/kg adsorbent) and breakthrough time (10.50 min) were obtained for the experimental region under consideration.

4. Conclusions

The influence of adsorption pressure and temperature in a CO₂ pre-combustion capture process was conducted in a fixed bed adsorption unit at pressures from 5 to 15 bar, and temperatures from 25 to 65 °C using a commercial activated carbon. Response surface methodology was used to evaluate the combined effect of the CO₂ partial pressure and the temperature on CO₂ capture capacity and breakthrough time. The CO₂ partial pressure was found to be the most influential variable. As it increased, both the CO₂ capture capacity and the breakthrough time linearly increased. On the contrary, as the temperature increased, both response variables decreased. No interaction effect between the two independent variables was detected. The maximum values of CO₂ capture capacity (3.96 mol/kg adsorbent) and breakthrough time (10.50 min) within the experimental region studied were obtained when capture was carried out at 25 °C and 3 bar of CO₂ partial pressure (total pressure of 15 bar). Further tests need to be conducted in order to study the influence of operating conditions on the adsorbent performance during the regeneration step. This work will contribute to the development of a suitable regeneration strategy in a pre-combustion capture process.

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Figure 1. Schematic of the experimental set-up for the column breakthrough measurements.

Figure 2. Sketch of the adsorption-desorption cycle configuration.

Figure 3. Example of a complete breakthrough experiment consisting of four consecutive adsorption-desorption cycles at 65 °C and 5 bar (20% CO₂ in feed gas): (1) initial drying step, (2) pre-conditioning step, (3) adsorption step and (4) desorption step.

Figure 4. Breakthrough curves of 20% CO₂ in feed gas at a varying adsorption temperature (a, b and c) and pressure (d, e and f).

Figure 5. Percentage of unused bed for the breakthrough experiments with activated carbon at varying adsorption temperatures and pressures.

Figure 6. Response surface and contour plots for CO₂ capture capacity and breakthrough time, t_b , as a function of the independent variables, P_{CO_2} and T .

Table 1. Physical properties of activated carbon and characteristics of the fixed-bed reactor

Norit R2030	
BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	942
Helium density (kg m^{-3})	2140
Apparent density (kg m^{-3})	845
Extrudate diameter (mm)	3
Particle porosity	0.61
Fixed-bed reactor	
Bed height (m)	0.108
Bed dead space (m)	0.095
Bed diameter (m)	0.009
Bed porosity	0.46
Mass of adsorbent (g)	3.22

Table 2. Independent variables and experimental values of the response variables for a three-level full factorial design

Run	Independent variables		Response variables	
	T (°C)	P _{CO2} (bar)	Capture capacity (mol CO ₂ /kg adsorbent)	Breakthrough time, t _b (min)
1	25 (-1)	1 (-1)	2.46	5.62
2	25 (-1)	2 (0)	3.02	8.15
3	25 (-1)	3 (+1)	3.98	10.5
4	45 (0)	1 (-1)	1.70	3.85
5	45 (0)	2 (0)	2.50	6.03
6	45 (0)	3 (+1)	3.32	8.81
7	65 (+1)	1 (-1)	1.35	3.18
8	65 (+1)	2 (0)	2.04	5.66
9	65 (+1)	3 (+1)	3.05	7.78
10	45 (0)	2 (0)	2.24	5.63
11	45 (0)	2 (0)	2.59	5.71
12	45 (0)	2 (0)	2.32	6.06
13	45 (0)	2 (0)	2.24	6.15
Central point mean	45	2	2.38	5.92

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

	Capture capacity (mol CO ₂ /kg adsorbent)				Breakthrough time. t _b (min)			
	Coded coefficient	Sum of squares	DF	<i>p</i> -value	Coded coefficient	Sum of squares	DF	<i>p</i> -value
Intersection	2.371	32.616	1	0.000	5.992	208.224	1	0.000
T	-0.503	1.520	1	0.000	-1.275	9.754	1	0.000
P _{CO2}	0.807	3.904	1	0.000	2.407	34.752	1	0.000
T·P _{CO2}	0.045	0.008	1	0.483	-0.070	0.020	1	0.594
T·T	0.175	0.085	1	0.048	0.724	1.448	1	0.002
P _{CO2} ·P _{CO2}	0.155	0.067	1	0.072	0.149	0.061	1	0.356
Model		5.676	5	0.000		46.556	5	0.000
Residual		0.103	7			0.439	7	
Total		5.780	12			46.996	12	
Lack of fit		0.002	3	0.993		0.227	3	0.360
Pure error		0.101	4			0.213	4	
R ²	0.982				0.991			
Adj-R ²	0.969				0.984			
AAD (%)	3.37				1.96

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