Title: Water vapour adsorption by a coffee-based microporous carbon: effect on CO₂ capture¹

Short title: Water vapour adsorption by a coffee-based carbon: effect on CO₂ capture

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Abstract

BACKGROUND: Carbon materials are appealing adsorbents for postcombustion CO₂ capture applications. In the present work, the adsorption of H₂O, which is an abundant component in flue gases, and its influence on the adsorption of CO₂ is evaluated using a microporous carbon.

RESULTS: The adsorption and desorption isotherms of H₂O at 12.5, 25, 50, 70 and 85 °C were obtained for relative pressures between 0 and 0.95. The average isosteric heat of adsorption of H₂O on PPC is 46 kJ mol⁻¹. The equilibrium of adsorption and desorption of H₂O on PPC can be reasonably well described by the DJD model in the entire temperature and pressure range evaluated. Breakthrough experiments carried out with synthetic flue gas showed that the adsorption of CO₂ is not hindered by H₂O at short adsorption times, relevant for the adsorption of CO₂. Moreover, PPC can be fully regenerated recovering its full adsorption capacity after extended exposure to humid gas.

CONCLUSIONS: Although the adsorption capacity of CO₂ can be reduced by the coadsorption of H₂O, this effect only becomes significant at long adsorption times. By appropriately selecting the adsorption time in the cyclic process design the concentration of CO₂ in the adsorbed phase can be maximized.

Keywords: adsorption, CO₂ capture, H₂O, activated carbon

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INTRODUCTION

Given the still dominant role of fossil fuels in primary energy consumption and the increasing global energy demand, carbon capture and storage (CCS) will play a critical role in delivering energy security and attaining the necessary CO₂ emissions reduction targets^{1, 2}. Adsorption processes are one of the separation technologies that are being considered for CO₂ capture applications³⁻⁵. Carbon-based materials are considered as one of the most promising adsorbents for CO₂ capture due to their low cost, tailored surface chemistry and pore size, and relative easiness for regeneration⁶. Moreover: carbon materials are hydrophobic, due to the low affinity of the polar water molecule for the carbon surface, and present high stability in moist conditions, which make these adsorbents appealing candidates for postcombustion CO₂ capture applications, in which the flue gas presents significant water content. In fact, H₂O is generally the third most abundant component of flue gases after N₂ and CO₂, followed by O₂. The actual content of H₂O in the gas to be decarbonized will depend on the process where it comes from (for example, the flue gas leaving a wet desulfurization unit in a coal power plant will be nearly saturated with water vapour) and its temperature (the lower the temperature the lower will be the absolute content of water vapour). Therefore the effect of water vapour on CO₂ capture is an important issue that needs to be addressed.

H₂O is a polar molecule which is strongly adsorbed by many inorganic adsorbents like zeolites. For this reason, the adsorption processes that consider the use of this type of adsorbents generally include a dehumidifying unit that uses alumina to remove water from the feed gas prior to enter the capture unit⁷ or a multilayer alumina-zeolite adsorber column⁸. The interaction of water molecules with the hydrophobic carbon surface is less favoured, especially at low relative pressures. This facilitates the regeneration of the carbon adsorbents working in humid conditions by vacuum swing adsorption (VSA)⁹⁻¹¹ or temperature aided vacuum swing adsorption (VTSA)^{11, 12}, eliminating the need of a dehydration unit with the subsequent operating and installation cost savings.

In this work, the adsorption of water vapour on a sustainable and inexpensive carbon adsorbent, PPC^{13, 14}, that has been obtained from an abundant residue from the food industry, coffee grounds, is evaluated. PPC has been already evaluated for the separation of dry CO₂/N₂ streams by VSA and VTSA showing promising results¹⁴. Here focus is placed in the adsorption of water vapour at conditions relevant to a postcombustion capture unit: the equilibrium of adsorption and desorption has been evaluated in static conditions in a wide temperature range, 12.5-85 °C, and up to high relative humidities. Most of the equilibrium data of water vapour on activated carbons that can be found in literature are limited to low temperatures, and the adsorption models frequently used to describe the equilibrium of adsorption are not valid at high relative pressures. To the authors knowledge, only one model has been proposed to cover the full relative pressure range of water adsorption and desorption of carbon adsorbents: the Horikawa-Do model (HD)¹⁵, which reduces to the model initially proposed by Do, Junpirom and Do (DJD) for microporous carbons¹⁶. Up to date, the majority of the published literature on CO₂ capture by adsorption deals with dry gas mixtures. The influence of H₂O on the CO₂ capture performance has only gained interest recently^{8-11, 17, 18}. In this work the effect of the coadsorption of water vapour over the adsorption of CO₂ on PPC has been evaluated under dynamic conditions using a fixed-bed adsorption unit and synthetic flue gas mixtures in the presence and absence of water vapour. To help with the interpretation of the experimental results the breakthrough curves obtained in humid conditions were simulated with Aspen Adsorption, using the DJD adsorption model parameters fitted to the equilibrium adsorption isotherms of H₂O.

EXPERIMENTAL SECTION

Materials

The adsorbent used in this work, PPC^{13, 14}, consists on cylindrical pellets with a diameter of 2.7 mm and an average height of 1.9 mm. It has been obtained from spent coffee grounds by

single-step activation with CO₂. PPC is a microporous carbon with a narrow micropore size distribution that has shown adequate properties as a CO₂ adsorbent at low partial pressures¹⁴. Further characterization details can be found elsewhere¹⁴.

Equilibrium of adsorption measurements

Water vapour adsorption and desorption isotherms at 12.5, 25, 50 70 and 85 °C were measured using a sorption analyser Hydrosorb 1000 HT from Quantachrome. Ca. 0.2 g of sample were outgassed *in-situ* under vacuum (≤ 10 mTorr) at 100 °C overnight in the same sample cell used for later analysis. The automated adsorption apparatus is provided with two pressure transducers of 100 and 1000 Torr (resolution: 0.01 % of full scale). The water reservoir and the dosing system are kept at a constant temperature of 100 °C, and the temperature of the sample cell during the analysis is controlled using a thermostatic bath circulator F25 from Julabo (resolution: 0.1 °C; temperature stability ± 0.03 °C).

Dynamic adsorption measurements

Breakthrough experiments were carried out using synthetic flue gas mixtures in the presence and absence of water vapour using a fixed-bed adsorption unit described elsewhere¹¹. The adsorber, a stainless steel column with an internal diameter of 9.12 mm placed in vertical position, was carefully packed with 3.5 g of PPC pellets.

The feed composition and its mass flow rate were analyzed prior to start the breakthrough measurement by-passing the adsorber by means of a transference valve. Once the composition of the mixture was stable, the transference valve was switched on ($t=0$) and the gas mixture was fed to the adsorber, which was initially regenerated and full of N₂. The temperature of the adsorber was kept constant at 25 °C during the full breakthrough experiment to avoid effects associated to the fluctuation of ambient temperature.

A series of breakthrough experiments (runs 1-3) were carried out at 1.5 bar and 25 °C using binary gas mixtures of N₂ and CO₂ and ternary mixtures with N₂, CO₂ and H₂O which composition resembled flue gas (16 % CO₂). The individual flow rate of N₂ and CO₂ fed to the

adsorber were kept constant for the 3 runs, although during run 2, N₂ was humidified prior to be mixed with CO₂. The adsorbent was regenerated with N₂ at 150 °C between consecutive runs. The total amount of CO₂ and H₂O adsorbed at a given time by PPC was calculated by means of a component mass balance to the unit and discounting the gas hold up in the void space (it was assumed ideal gas behaviour).

The experimental breakthrough experiments were simulated using Aspen Adsorption V8.0. Detailed information of the simulation environment can be found elsewhere¹⁹. Figure 1 shows the flowsheet used to run the simulations, which was designed to emulate the experimental unit¹¹. The flowsheet consists on a series of individual block or models (represented by Feed, Vt1, Adsorber, Vt2, HD and Effluent in Figure 1) that are interconnected by material streams. Adsorber represents the adsorbent bed (height: 14.7 cm; internal diameter of the adsorber column: 9.12 mm; interparticle voidage: 0.51; intraparticle voidage: 0.6; bulk density: 365 kg m⁻³). The model is constituted by a set of partial differential equations that represent the momentum, energy and material balances across the column. The main model equations are shown in the Appendix. The following assumptions were made: isothermal condition, negligible radial mixing, and pressure drop given by the Ergun equation. Axial dispersion was estimated locally for the superficial velocity of the gas phase using an appropriate correlation (*convection with estimated dispersion*¹⁹). The molecular diffusivities of the components in the gas mixture were calculated for the feed composition using the Wilke method²⁰ and the Chapman-Enskog theory²¹ and were assumed approximately constant. It was assumed that the main transfer resistance inside the pellets occurred in the micropores and the material balance at the particle level was solved assuming that the effective adsorbed phase diffusion coefficient was approximately constant throughout a single pellet (*Particle MB*¹⁹). Specifically designed user procedures were created to describe the equilibrium of adsorption (see the Results section for further details). The spatial derivatives were discretized using the upwind differencing scheme 1 method (USD1, first order). The adsorber height was divided into 30

nodes and the pellet radius into 5 nodes. The small void volumes at the inlet and outlet of the adsorber which are full of N₂ at t=0, were represented by gas void tank models¹⁹ (labelled as Vt1 and Vt2, in Figure 1) with the following volumes and initial conditions: Vt1=1.17 cm³; Vt2=0.65 cm³; $y_{vt1,N_2,t=0} = y_{vt2,N_2,t=0} = 1$. HD is a gas void tank model that accounts for the void volume of the unit that is full of feed gas at t=0: HD= 193 cm³; $y_{HD,i,t=0} = y_{feed,i}$.

RESULTS AND DISCUSSION

Equilibrium of adsorption

Figure 2 shows the adsorption and desorption isotherms of water vapour on PPC at 12.5, 25, 50, 70 and 85 °C. The adsorption measurements (A) are represented by filled symbols and the desorption measurements (D) by empty symbols.

The adsorption isotherms present a likewise behaviour with two uptake zones: the first, that takes place at very low relative pressures, is generally attributed to the adsorption of water molecules on the oxygen²² and nitrogen^{23, 24} surface functional groups, and also on the inorganic matter^{25, 26} present at the pore entrances. The total content of these primary adsorption sites on PPC is relatively large: 9 wt. % O, 4.7 wt % N and 4.6 wt % inorganic matter (dry basis), which makes the initial upswing of the adsorption isotherms significant. Water adsorption proceeds by H-bonding on top of adsorbed water molecules, forming clusters of increasing size²⁷. When the clusters attain a critical size, they gain sufficient dispersive force to enter the micropores²⁷, which leads to the second (and largest) uptake zone. Micropore filling occurs at relative pressures between 0.1 and 0.4, which is relatively low compared to other carbons^{11, 28}. This is attributed to the narrow pore size of PPC¹⁴ and to the presence of primary adsorption sites on its surface that contributes to shift the condensation pressure to lower values²⁹. The hysteresis loop observed at all the temperatures between the adsorption and desorption branches of the isotherms is quite narrow, which is also attributed to the narrow pore size of PPC^{30, 31}. If the isotherms are depicted as amount of H₂O adsorbed *versus* relative pressure, they practically overlap, which means that the adsorption of water vapour on PPC is

practically unaffected by temperature. This is in good agreement with the observations made by Horikawa *et al.* for microporous carbons in the temperature range between -5 and 25 °C³².

The maximum adsorption capacity of PPC, near 12 mmol g⁻¹, is relatively low compared to activated carbons with higher pore volume: it is nearly half of that of the commercial activated carbon BPL³³ or that of a biomass-based carbon previously evaluated in our group¹¹. Compared to zeolites, the main difference comes from the shape of the adsorption isotherms: in the first case, they present high adsorption capacities from very low relative pressures. For example, zeolite 13 X presents an adsorption capacity of 12.1 mmol g⁻¹ at 25 °C and at a relative pressure of only 0.13³⁴, while the adsorption capacity of PPC at the same temperature and pressure is four times smaller.

The isosteric heat of adsorption of water vapour on PPC was estimated from the Clausius Clapeyron plots ($\ln P$ vs. $1/T$). The isosteres were obtained by linear interpolation of the adsorption and desorption equilibrium data measured at 12.5, 25, 50 70 and 85 °C. These showed linear trend in the evaluated temperature range (correlation coefficients ≥ 0.994), which indicates that the isosteric heat of adsorption can be considered independent of temperature and that the Clausius Clapeyron relation is valid. Figure 3 shows the isosteric heat of adsorption calculated from the adsorption and desorption isotherms as a function of loading. The values obtained from the adsorption data are very close to those obtained from the desorption data. The isosteric heat of adsorption presents a nearly constant pattern with loading, except for the highest loadings, when it decreases to meet the average latent heat of vaporization in the temperature range between 12.5 and 85 °C (43 kJ mol⁻¹)³⁵. The net heat of adsorption, defined as the difference between the average isosteric heat of adsorption and the average heat of vaporization for the temperature interval evaluated, is only 3 kJ mol⁻¹, which is an indicative of the weak nature of the forces involved in the physisorption process. The average isosteric heat of adsorption for loadings between 1.1 and 11.3 mmol g⁻¹, is 46 kJ mol⁻¹, which is significantly lower than the isosteric heat of adsorption of H₂O on zeolite 13X (54-

62 kJ mol⁻¹ for loadings between 3 and 12 mmol g⁻¹)³⁶. The lower the isosteric heat of adsorption the lower energy will be required to regenerate the adsorbent.

Relatively simple adsorption models, like the Toth equation, which is useful to describe the equilibrium of adsorption of CO₂ and N₂ on PPC¹⁴, fails to describe the equilibrium of adsorption of H₂O on the same adsorbent. However, the model proposed by Do, Junpirom and Do (DJD)¹⁶ for the adsorption of water vapour on microporous carbons describes adequately the equilibrium of adsorption (and desorption) of water vapour on PPC in the entire pressure and temperature range evaluated. The DJD model equations are shown below (Equations 1 and 2):

$$C_{DJD,A} = S_0 \frac{k_f \sum_{n=1}^m n x^n}{1 + K_f \sum_{n=1}^m x^n} + C_{\mu s} \frac{k_{\mu} \sum_{n=\alpha_{\mu}+1}^m x^n}{k_{\mu} \sum_{n=\alpha_{\mu}+1}^m x^n + \sum_{n=\alpha_{\mu}+1}^m x^{n-\alpha_{\mu}}} \quad (1)$$

$$C_{DJD,D} = S_0 \frac{k_f \sum_{n=1}^m n x^n}{1 + k_f \sum_{n=1}^m x^n} + C_{\mu s} \frac{k_{\mu} (1 + K_{R\mu}) \sum_{n=\alpha_{\mu}+1}^m x^n}{k_{\mu} (1 + K_{R\mu}) \sum_{n=\alpha_{\mu}+1}^m x^n + \sum_{n=\alpha_{\mu}+1}^m x^{n-\alpha_{\mu}}} \quad (2)$$

$$MSE_A = \frac{\sum_{i=1}^N (C_{exp,A} - C_{DJD,A})}{N_A} \times 100 \quad (3)$$

$$MSE_D = \frac{\sum_{i=1}^N (C_{exp,D} - C_{DJD,D})}{N_D} \times 100 \quad (4)$$

$C_{DJD,A}$ is the total amount of H₂O adsorbed at a relative pressure x corresponding to the adsorption branch, S_0 is the concentration of primary adsorption sites on the carbon surface, K_f is the chemisorption equilibrium constant, m represents the maximum number of water molecules that could form around one single functional group, $C_{\mu s}$ is the saturation concentration in the micropores, K_{μ} is the micropore equilibrium constant, α_{μ} represents the critical size of the water cluster to enter the micropores, $C_{DJD,D}$ is the total amount of H₂O that remains adsorbed at a relative pressure x corresponding to the desorption branch, and $K_{R\mu}$ is the relaxation equilibrium constant for water desorption from the micropores¹⁶. The DJD model parameters S_0 , K_f , α_{μ} , $C_{\mu s}$, and K_{μ} were adjusted at each temperature to minimize the mean squared error (MSE_A) between the experimental adsorption data and the DJD adsorption model (Equation 3). The value of m was set to: $m = \alpha_{\mu} + 1$ ¹⁵. The relaxation equilibrium constant

for water desorption from the micropores, $K_{R\mu}$, was fitted to minimize the mean squared error (MSE_D) between the experimental desorption data and the DJD desorption model (Equation 4). The so optimized values of the DJD model can be found in Table 1. The value of α_μ is intrinsically related to the pore size¹⁵: the optimized value for PPC, $\alpha_\mu = 3$, is rather small in comparison with a previously evaluated biomass-based carbon with a wider pore size¹¹. The average O-O separation in the gas phase cyclic water trimer structure is 0.28 nm³⁷. The packing fraction, calculated from the ratio of the saturation concentration of water in the micropores, $C_{\mu s}$, to the hypothetical case where all the micropore volume was filled with liquid water, falls within 0.59-0.66 which is very close to the values reported for other microporous carbons^{11, 15}. The concentration of primary adsorption sites available for water adsorption on the carbon surface, S_o , is well below the physical upper limit, given by the total concentration of oxygen, nitrogen and inorganic matter (S_o represents only 24-32% of the total oxygen content of PPC). The chemisorption equilibrium constant, K_f , and the micropore equilibrium constant, K_μ , show a decreasing trend with temperature, as expected for physisorption processes. In general $MSE_D > MSE_A$ because only one parameter was fitted to reproduce the experimental desorption isotherms. Figure 4 shows the goodness of fit of the DJD model to the adsorption and desorption isotherm of H₂O on PPC at 25 °C. The DJD model with the optimal parameters shown in Table 1 adequately describes the equilibrium of adsorption and desorption in the entire pressure range. Similarly, good agreement between the model and the experimental measurements were obtained at the rest of the temperatures evaluated (see values of MSE_A and MSE_D in Table 1), except for the desorption branch of H₂O at 85 °C that presents a slightly greater deviation in the upper part of the hysteresis loop.

Breakthrough experiments

Figure 5a compares the breakthrough curves of CO₂ obtained in the absence and presence of H₂O in the feed gas (runs 1-3). When the synthetic flue gas mixture is fed to the adsorber at $t=0$, the molar fraction of CO₂ in the effluent starts to decay due to the preferential adsorption

of CO₂ over N₂ (note that the dead volume of the unit located between the adsorber and the analyser, represented by HD in Figure 1, was initially full of feed gas which prevents the flow rate of CO₂ in the effluent to be zero at t=0). The molar fraction of CO₂ in the effluent goes through a minimum at near 3 min, and then starts to increase again (breakthrough) to meet the feed value in approximately 11 min. At this point, all the adsorbent has apparently reached the equilibrium of adsorption with CO₂. It is important to highlight that the CO₂ breakthrough curves obtained in the absence of water vapour in the feed (runs 1 and 3), carried out before and after the wet run, respectively, overlap with the breakthrough curve of CO₂ obtained using the humidified feed gas (run 2). This indicates not only a good repeatability and reproducibility of the experimental results, but also that the adsorbent has recovered full adsorption capacity after regeneration, even after extended exposure to humid conditions. Moreover, water vapour does not reduce the adsorption capacity of CO₂ at short adsorption times: see Figure 5b, where the cumulative amount of CO₂ adsorbed during the first 15 min of the wet run is compared with those of the dry runs. This is important, as the cyclic adsorption processes that would be used to carry out the separation of CO₂ from flue gases will use very short step times (of the order of a few s or min) in order to increase throughput.

The effect of the coadsorption of H₂O and CO₂ at longer adsorption times was assessed by continuing the wet breakthrough experiment (run 2) until the adsorbent was apparently saturated with H₂O (the experiment was stopped after 523 min, once the relative humidity of the effluent stabilised at 52 %). Figure 6a shows the history of the molar fractions of CO₂ and H₂O in the effluent during run 2. At the beginning of the experiment, both CO₂ and H₂O are adsorbed: the effluent is temporarily enriched in N₂ until the mass transfer zones of CO₂ and H₂O reach the adsorber outlet. From this point (breakthrough), they start to increase, approaching a constant pattern once the adsorbent becomes saturated. This phenomenon is much faster in the case of CO₂, which breaks through the adsorber in approximately 3 min, while H₂O takes above 200 min. In the experimental conditions evaluated, PPC became

saturated in approximately 450 min. Note that the breakthrough curves of CO₂ and H₂O show a different topology: H₂O shows a two-step increase instead of the single-step shown by CO₂. This is related to the equilibrium of adsorption of each species (type V-VI adsorption isotherms *versus* type I-II).

The cumulative amount of CO₂ and H₂O adsorbed per gram of PPC during run 2 is shown in Figure 6b. The amount of CO₂ adsorbed goes through a maximum for adsorption times between 10 and 24 min that matches the amount adsorbed during the dry runs (see Figure 5b). However, as time proceeds, the amount of CO₂ adsorbed starts to decrease due to the preferential adsorption of the slower moving H₂O, which progressively displaces part of the CO₂ initially adsorbed. The amount of H₂O adsorbed increases up to 10.5 mmol g⁻¹ and then stabilizes. Likewise, the amount of CO₂ adsorbed is progressively reduced until it stabilizes at a value of 0.6 mmol g⁻¹. At this point the adsorbent bed is considered to be in equilibrium with the humid feed gas. The amount of H₂O adsorbed is in good agreement with the equilibrium measurements carried out with pure H₂O at 25 °C (Figure 4). In the case of CO₂, the amount that remains adsorbed after 523 min of continued adsorption in humid conditions represents approximately 40% of the pure component adsorption capacity.

To better understand the adsorption process, the breakthrough curves were simulated using Aspen Adsorption software (see details in the experimental section). The equilibrium of adsorption of H₂O was described making use of the pure component DJD model. Although the effective diffusivity is known to vary with the adsorbed phase concentration^{38, 39}, as a first approximation it was assumed constant. The self-diffusion coefficient of water is dependent on pore size. Dubinin *et al.*⁴⁰ measured the self-diffusion coefficient of water on several activated carbons (AC) with different pore size (average micropore widths between 0.4 and 1.5 nm) using NMR pulsed field gradient technique, and found that the self-diffusivity of water increases with pore size. Taking into consideration the correlation between the pore size and the diffusivity measurements of Dubinin *et al.*⁴⁰, a diffusivity coefficient of 2.1E-10 m² s⁻¹ could

be expected for PPC (average micropore size of 1 nm, based on N₂ adsorption at -196 °C). The effect of confinement on the self-diffusivity of water on single wall carbon nanotubes (SWCNT) of effective diameter between 0.9 and 2.4 nm has also been evaluated using molecular simulation⁴¹. According to this study, as the effective diameter of the SWCNT increases, the self-diffusivity of water tends to that of bulk water (2.5E-9 m² s⁻¹); the value given for (10,10) SWCNT, 1.2E-9 m² s⁻¹, is one order of magnitude higher than that measured by Dubinin *et al.* for an AC with a similar pore size⁴⁰. This difference can be attributed to the heterogeneity of AC compared to the smooth surfaces of SWCNTs. Figure 7a compares the experimental breakthrough curve of H₂O with the simulation results obtained using different effective diffusivities for H₂O. The difference between the experimental data and the simulations for the initial decay of concentration is attributed to the non-ideal mixture that takes place in the void volume of the unit (not taken into account by the gas_tank_void model, HD). None of the aforementioned diffusivity values predicted accurately the full shape of the breakthrough curve: the highest value evaluated, taken from the molecular simulations carried out with SWCNT, reproduced better the breakthrough time but predicted a steeper breakthrough, while the lowest value, taken from the AC measurements, reproduced better the final part of the curve, but predicted a premature breakthrough. An intermediate diffusion coefficient, 4E-10 m² s⁻¹, close to the AC measurements, was found to reproduce the whole curve the best although slightly shifted to lower times. The delay in the experimental signal compared to the simulation case is attributed to poor mixing in the humidity probe housing (this will be amended in future measurements).

In the case of CO₂, the pure component adsorption model (Toth)¹⁴ was corrected to account for the observed decrease in the adsorption capacity due to the adsorption of H₂O (Figure 6b). As a first approximation, the equilibrium of adsorption of CO₂ was assumed to follow the expression:

$$C_{\mu,CO_2} = C_{\mu,CO_2}^* - xC_{\mu,H_2O} \quad (5)$$

where C_{μ,CO_2} is the amount of CO_2 adsorbed locally, C_{μ,CO_2}^* is the local equilibrium capacity according to the pure component adsorption model, and C_{μ,H_2O} is the amount of H_2O adsorbed locally by PPC. The value of the parameter x was estimated using the multicomponent equilibrium data extracted from run 2: $x=0.08$. The effective diffusivity of CO_2 was fitted to reproduce the experimental breakthrough curve: the lowest value that gave a good fit of the curve (see Figure 7b) was: $6E-8 \text{ m}^2 \text{ s}^{-1}$. This value is somewhat higher than that reported for the surface diffusion of CO_2 in the commercial activated carbon BPL at the same temperature ($1.4E-8 \text{ m}^2 \text{ s}^{-1}$)⁴². Moreover, the diffusivity of CO_2 is two orders of magnitude higher than that of H_2O . The higher diffusivity of CO_2 will facilitate the kinetic separation of CO_2 from H_2O : by selecting short adsorption times, which are to be expected in rapid swing cyclic adsorption processes, the adsorption of CO_2 will be little influenced by the delayed front of H_2O .

One of the advantages of simulation is that it allows us to observe what is happening inside the adsorber at a given time. Figure 8 shows the profile of the molar fractions and adsorbed amount of H_2O and CO_2 along the axial position in the adsorber at three different times: just before and after the breakthrough of CO_2 ($t = 2.2 \text{ min}$ and $t = 4.0 \text{ min}$, respectively), and at equilibrium ($t=523.0 \text{ min}$). As shown in the figure, at short adsorption times the gas phase inside the adsorber is essentially free of H_2O , and most of the adsorbent bed is in equilibrium with the dry gas. The concentration of CO_2 in the adsorbed phase reaches the maximum just after the breakthrough curve. However, as the water concentration front moves through the adsorbent bed, part of the initially adsorbed CO_2 is desorbed. At sufficient long adsorption times, once the adsorber reaches equilibrium with the humid feed, the composition of the gas phase inside the adsorber is equal to that of the feed. Therefore, by appropriately selecting the step times during the design of an adsorption cyclic process, it may be possible to maximize the amount of CO_2 adsorbed and minimize the coadsorption of H_2O ; this will improve the purity of the product, the throughput of the process and also facilitate the ulterior

regeneration of the adsorbent.

CONCLUSIONS

The equilibrium of adsorption and desorption of H₂O on microporous carbon PPC has been evaluated in the temperature range between 12.5 and 85 °C. This can be reasonably well described by the DJD model in the entire relative pressure range. The adsorption of H₂O on PPC shows a weak dependence with temperature. The maximum adsorption capacity of H₂O on PPC is lower than for other activated carbons with higher pore volume, which is advantageous, as less H₂O will be coadsorbed with CO₂ at the high relative humidities that can be expected in post-combustion applications. The lower uptake of H₂O at low relative pressures and the smaller heat of adsorption of H₂O on PPC compared to inorganic adsorbents will facilitate the regeneration of the adsorbent by smaller pressure or temperature swings.

The water hold up needs to be addressed in adsorption processes under humid conditions, as this can reduce the adsorption capacity for CO₂. However, the adsorption of CO₂ on PPC showed not to be hindered by the presence of H₂O in the feed gas at short adsorption times, relevant for the adsorption of CO₂. Moreover, PPC recovered its full adsorption capacity after regeneration. By appropriately selecting the adsorption time in the cyclic process design we can maximize the concentration of CO₂ in the adsorbed phase and minimize the amount of water adsorbed, thus facilitating the subsequent regeneration of the adsorbent, and improving product purity and throughput.

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Tables

Table 1. DJD model parameters

T (°C)	S_0 (mmol g ⁻¹)	K_f	α_μ	$C_{\mu s}$ (mmol g ⁻¹)	K_μ	$K_{R\mu}$	MSE_A	MSE_D
12.5	1.30	898	3	8.15	117	0.80	2	2
25	1.50	126	3	8.45	77	0.68	3	6
50	1.51	53	3	8.09	54	0.42	4	5
70	1.32	63	3	8.05	52	0.49	3	5
85	1.73	53	3	7.40	43	1.00	2	11

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Figure 1. Flowsheet configuration used to run the simulation of the experimental breakthrough curves using Aspen Adsorption. Vt1, Vt2 and HD are gas_tank_void models that represent the void volume of the experimental unit, and Adsorber is a gas_bed model that represents the adsorber column of the experimental unit. These are connected by material streams to the Feed, represented by a gas_Feed model, and the Effluent, represented by a gas_Product model.

Figure 2. Water vapour adsorption isotherms at 12.5, 25, 50, 70 and 85 °C on carbon PPC (filled symbols correspond to adsorption data (A) and empty symbols to desorption data (D))

Figure 3. Isostatic heat of adsorption of H₂O on PPC as a function of loading, estimated from the experimental adsorption and desorption isotherms measured at 12.5, 25, 50, 70 and 85 °C.

Figure 4. Adsorption and desorption isotherms of H₂O on PPC at 25 °C: the symbols represent experimental data and the lines the DJD model.

Figure 5. Effect of H₂O on the adsorption of CO₂ in the short time scale: (a) comparison of CO₂ breakthrough curves carried out under dry (run 1 and run 3) and humid conditions (run 2); (b) cumulative amount of CO₂ adsorbed per gram of PPC *versus* time for runs 1-3.

Figure 6. Run 2: (a) experimentally measured breakthrough curves of H₂O and CO₂; (b) cumulative amount of CO₂ and H₂O adsorbed per gram of PPC *versus* time.

Figure 7. Comparison of simulated and experimental breakthrough curves of (a) H₂O and (b) CO₂.

Figure 8. Snapshots of the profiles of H₂O and CO₂ inside the adsorber at different adsorption times (2.2, 4.0 and 523.0 min) obtained by simulation; (a) molar fractions; (b) amount adsorbed per gram of PPC.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8