12th International Chemical and Biological Engineering Conference

BOOK OF

EXTENDED ABSTRACTS
This volume contains the communications presented at the 12th International Chemical and Biological Engineering Conference - CHEMPOR 2014, held in Porto, Portugal, between September 10th and 12th, 2014.

CHEMPOR 2014 was organized by
FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO
&
ORDEM DOS ENGENHEIROS

Title: Book of Extended Abstracts of the 12th International Chemical and Biological Engineering Conference - CHEMPOR 2014

Published by:
Faculdade de Engenharia
Universidade do Porto

http://chempor.ordemengenheiros.pt


First edition August 2014
ISBN: 978-972-752-170-8

FEUP Edições

http://feupedicoes.fe.up.pt

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Water vapour adsorption by a coffee-based microporous carbon: effect on CO\(_2\) capture

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Carbon materials are appealing adsorbents for postcombustion CO\(_2\) capture applications due to their low cost and high stability in flue gas conditions. In the present work, the adsorption of H\(_2\)O and CO\(_2\) on microporous carbon PPC, obtained from spent coffee, is evaluated. Despite its intrinsic hydrophobicity, the maximum equilibrium adsorption capacity of PPC in the temperature range between 25 and 50 °C follows the order: H\(_2\)O>CO\(_2\)>N\(_2\). On the other hand, dynamic adsorption experiments carried out with synthetic flue gas mixtures, showed that the adsorption of CO\(_2\) is not hindered by the slower moving H\(_2\)O adsorption front. Moreover, PPC can be fully regenerated recovering its full adsorption capacity after repeated exposure to humid gas. However, the coadsorption of water vapour needs to be addressed during the CO\(_2\) capture process design.

**Introduction**

It is known that carbon materials are hydrophobic, due to the low affinity of the polar water molecule for the carbon surface. This property, together with the high stability of carbon materials in moist conditions and their low cost, make these adsorbents appealing candidates for postcombustion CO\(_2\) capture applications, in which the flue gas present significant water content (H\(_2\)O is the third bulk component after N\(_2\) and CO\(_2\)). The effect of water vapour on CO\(_2\) capture is an important issue that needs to be addressed.

**Methods**

Adsorbent PPC (patent application filed) is a pelletised microporous carbon that has been obtained from spent coffee grounds by single-step activation with CO\(_2\).

Water vapour adsorption isotherms at 25 and 50 °C were obtained up to the corresponding saturation pressure in a water vapour sorption analyser Hydrosorb 1000 from Quantachrome. N\(_2\) and CO\(_2\) adsorption isotherms at 25 and 50 °C were measured using an automated analyser TriStar 3000 from Micromeritics.

Breakthrough experiments were carried out using synthetic flue gas mixtures in the presence and absence of water vapour using the fixed-bed adsorption unit shown in Figure 1. The gas mixture was prepared by-passing the adsorber (transfer valve in position 2). Once the composition of the mixture was stable, the valve was switched to position 1 and the gas was fed to the adsorber initially regenerated and full of N\(_2\) (or He). The detailed description of the adsorption unit can be found elsewhere [1].

**Results and discussion**

Figure 2 shows the adsorption isotherms of water vapour at 25 and 50 °C on PPC. They present a likewise behaviour, with two uptake zones: the first, that takes place at low relative pressures, is related with the adsorption on the surface functional groups (mainly N and O). Water adsorption proceeds by H-bonding on adsorbed water molecules, forming clusters of increasing size. The second (and largest) uptake zone is due to micropore filling that occurs by the growth of the water clusters. A narrow hysteresis loop can be observed between the adsorption and desorption branches. This topology is different from the single uptake at low relative pressures shown by zeolites and alumina (adsorption isotherms of Type I and II, respectively).

As can be seen from Figure 2, the DJD model [2] describes adequately the equilibrium of adsorption (and desorption) of water vapour on the microporous PPC carbon in the entire relative pressure range.
Figure 2. Water vapor adsorption isotherms at 25 and 50 °C on carbon PPC.

Figure 3 shows the adsorption isotherms of CO$_2$ and N$_2$ at 25 and 50 °C. CO$_2$ adsorption isotherms are of Type I, while the adsorption isotherms of N$_2$ present a nearly linear topology. The adsorption capacity for CO$_2$ is significantly higher than that for N$_2$, in the entire pressure and temperature range evaluated, due to the higher quadrupole moment of the CO$_2$ molecule. The equilibrium of adsorption of CO$_2$ can be adequately described by the relatively simple Toth model (represented by the solid lines in Figure 3).

Figure 3. CO$_2$ and N$_2$ adsorption isotherms at 25 and 50 °C on carbon PPC.

A series of breakthrough experiments (runs 1-3) were carried out at 150 kPa and 25 °C using synthetic flue gas mixtures. Runs 1 and 3 were carried out using a dry feed gas with 84 % N$_2$ and 16 % CO$_2$, and run 2 was carried out with a wet gas containing 83 % N$_2$, 16 % CO$_2$ and 1 % H$_2$O (relative humidity: 70 %). The flow rates of N$_2$ and CO$_2$ fed to the adsorber were kept equal for the 3 runs (total molar flow rate: 8.2 mmol min$^{-1}$), although in run 2 the N$_2$ stream was scrubbed in distilled water prior to mix with CO$_2$. The adsorbent was regenerated with N$_2$ at 150 °C between runs.

Figure 4 compares the CO$_2$ breakthrough curves obtained in the absence and the presence of H$_2$O in the feed gas. When the gas mixture is fed to the adsorber at t=0 (transfer valve switched from position 2 (by-pass) to position 1 (adsorber)), the molar flow rate of CO$_2$ in the effluent starts to decrease due to adsorption. The outlet flow rate of CO$_2$ goes through a minimum at near 3 min in the experimental conditions evaluated, and then starts to increase again, meeting that of the feed in less than 10 min due to the saturation of the adsorbent. Note that the curves of runs 1 and 3, obtained before and after the wet run are similar, which indicates reproducibility of the results, but also that the adsorbent has recovered full adsorption capacity after regeneration. Moreover: no significant differences are observed between the wet and the dry runs, which indicates that water vapour is not significantly hindering the adsorption of CO$_2$.

Figure 4. Comparison of the CO$_2$ breakthrough curves of runs 1-3.

Figure 5 shows the history of the effluent composition during run 3. The effluent is initially enriched in N$_2$ due to the preferential adsorption of CO$_2$ and H$_2$O: the molar fraction of N$_2$ in the effluent goes through a maximum at near 3 min (simultaneous to the minimum in the molar fraction of CO$_2$) and then decreases again to meet the feed value. On the other hand, the molar fraction of water vapour in the effluent reaches its minimum value only after 200 min. From this point on, the water content in the effluent increases.
again, showing a two-step like behaviour, instead of the single-step increase shown by CO₂. The shape of the breakthrough curves is intrinsically related to the equilibrium of adsorption.

![Breakthrough curves](image)

**Figure 5.** Breakthrough experiment carried out at 150 kPa and 25 °C with 8.3 mmol min⁻¹ of a mixture containing 83 % N₂, 16 % CO₂ and 1 % H₂O (run 2).

A fourth breakthrough experiment (run 4) was carried out at 130 kPa and 25 °C with a gas mixture containing 80 % N₂, 14 % CO₂, 4 % O₂ and 2 % H₂O and a total molar flow rate of 2.6 mmol min⁻¹. The adsorber was initially regenerated and full of He. Results are shown in Figure 6, where the molar flow rate of each species in the effluent has been divided by the flow rate of each species in the feed to facilitate the comparison. O₂ and N₂ are the less adsorbed species, and reach the adsorber outlet approximately at the same time. When the CO₂ front reaches the adsorber outlet (see the inflection point in the CO₂ curve at near 12 min), a small roll-up is observed in the O₂ and N₂ curves. After approximately 30 min, the molar flow rates of N₂, O₂ and CO₂ in the effluent meet the feed values, while the molar flow rate of H₂O in the effluent continues to present a downward trend due to adsorption.

![Breakthrough curves](image)

**Figure 6.** Breakthrough experiment carried out at 130 kPa and 25 °C with 2.6 mmol min⁻¹ of a mixture containing 80 % N₂, 14 % CO₂, 4 % O₂ and 2 % H₂O (run 4).

In the breakthrough experiments carried out (runs 1-4), the adsorbent was initially free of CO₂ and H₂O. In these conditions, the adsorption capacity of CO₂ was not significantly reduced by the slower moving H₂O front. However, in a cyclic separation process, where the regeneration of the adsorbent is not complete, the coadsorption of water vapour can reduce the working capacity of CO₂ due to water hold up. Therefore the adsorption of water vapour needs to be addressed in the separation process design.

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

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