Evaluation of the cyclic capacity of low-cost carbon adsorbents for post-combustion CO$_2$ capture

M.G. Plaza, C. Pevida, J.J. Pis, F. Rubiera

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

Abstract

The CO$_2$ capture performance in post-combustion conditions (CO$_2$ diluted in nitrogen at near atmospheric pressure) of an aminated biomass-based carbon is compared to that of two commercial activated carbons. All the evaluated samples showed selectivity for CO$_2$ over N$_2$, being able to separate a binary mixture of CO$_2$ and N$_2$, and were easily regenerated by raising the temperature up to 373 K. The aminated carbon showed superior CO$_2$ adsorption capacity at low CO$_2$ partial pressures, leading to a better capture performance in a simple TSA cycle configuration without presenting any signs of deactivation over 40 cycles.

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Keywords: adsorption; activated carbon; CO$_2$ capture; surface modification

1. Introduction

CO$_2$ capture and storage (CCS) will need to play a critical role if the mid-to-long-term CO$_2$ reduction targets are to be met, given the current fossil fuel-based energy scenario. Among CCS, three main carbon capture technologies are identified: post-combustion, pre-combustion and oxy-fuel combustion. This work deals with the post-combustion case, in which CO$_2$ needs to be separated from the flue gases produced upon fuel combustion. The low partial pressure of CO$_2$ in the flue gas hinders the separation. Chemical absorption with aqueous solution of amines has been pointed out as the preferred technology. However, the regeneration of these solvents, which need to be diluted to avoid corrosion problems, is energy intensive, and much effort is being done in seeking alternative technologies with lower energy penalties.

Adsorption is a well developed separation technology with potential to reduce the cost of post-combustion capture compared to amine scrubbing [1-5]. Two main adsorption technologies are being considered for the post-combustion capture case: pressure swing adsorption (PSA) and temperature swing adsorption (TSA). The difference between both technologies is the way in which the adsorbent is regenerated: in PSA, the pressure of the adsorption bed is reduced, whereas in TSA, the temperature is raised while pressure is maintained approximately constant.

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1 Corresponding author. Tel.: +34 985119090; fax: +34 985297662.
E-mail address: frubiera@incar.csic.es.

doi:10.1016/j.egypro.2011.01.178
Usually, the term vacuum swing adsorption (VSA) is used to refer to the special PSA case where the desorption pressure is below atmospheric. Within TSA technologies, when the solid is heated by the Joule effect, the term electrical swing adsorption (ESA) is generally preferred. Independently of the regeneration strategy, the primary requirement to develop an efficient adsorption process is to find an adequate adsorbent with high capacity and CO₂ selectivity, but also stable to flue gases components and to long lasting cycling. The vast majority of studies dealing with CO₂ post-combustion capture by PSA or TSA technologies use zeolites as adsorbent [3-10]. However, activated carbons present important advantages over zeolites, such as significant lower cost, easier regeneration, hydrophobic character, etc. Our group has dealt with the preparation of carbon adsorbents for CO₂ capture applications over recent years [11-19]. In this work, one of the carbon adsorbents that had shown promising characteristics in previous studies is evaluated and compared with two commercial activated carbons for the separation of CO₂ from a N₂/CO₂ binary mixture, representative of post-combustion conditions.

2. Experimental

The commercial activated carbons, from now on referred by C and R, were supplied by Norit. C is a superactivated carbon, with the highest surface area of the series (see Table 1), produced from wood by the phosphoric acid process. R is a steam activated peat-based carbon, with a narrower pore size distribution. A detailed textural characterization of these carbons can be found elsewhere [12]. Sample A has been produced from an agricultural byproduct, by a first step of carbonization followed by amination (see reference [18] for further details). Table 1 summarizes the main physical properties of the studied adsorbents.

Figure 1 shows the CO₂ and N₂ equilibrium adsorption isotherms at 303 K up to 130 kPa for the three materials under study, obtained in a volumetric apparatus TriStar 3000. The three carbons present significantly higher adsorption capacity for CO₂ than for N₂ (high CO₂/N₂ equilibrium selectivity), and thus seem adequate candidates to carry out CO₂/N₂ separation. Note that carbon C presents the lowest adsorption capacity of the series in spite of its high surface area. Moreover, although sample R presents a slightly higher CO₂ adsorption capacity than A at atmospheric pressure, it is the latter which presents the highest CO₂ adsorption capacity at lower pressures (post-combustion conditions).

Table 1 Physical properties of the evaluated adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>C</th>
<th>R</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>1361</td>
<td>942</td>
<td>588</td>
</tr>
<tr>
<td>He density (kg m⁻³)</td>
<td>1512</td>
<td>2136</td>
<td>1902</td>
</tr>
<tr>
<td>Hg density at 0.103 MPa (kg m⁻³)</td>
<td>402</td>
<td>850</td>
<td>760</td>
</tr>
<tr>
<td>Particle void fraction</td>
<td>0.74</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>Bed density (kg m⁻³)</td>
<td>196</td>
<td>427</td>
<td>399</td>
</tr>
<tr>
<td>Bed void fraction</td>
<td>0.47</td>
<td>0.50</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Figure 1 Equilibrium adsorption isotherms of carbons C, R and A at 303 K up to 113 kPa: a) CO₂; b) N₂.
Fixed-bed adsorption experiments were conducted in a purpose built one-column adsorption unit (see Figure 2) consisting in a stainless steel reactor (157 mm height, 9 mm inner diameter) equipped with pressure and temperature control. CO₂ and N₂ flow rates were adjusted by means of accurate mass flow controllers, and mixed in a helicoidal distributor before entering the bed. The temperature of the bed was monitored continuously by means of a K-type thermocouple placed axially in the solids bed, at 45 mm from the bottom porous plate. It was controlled automatically by coupling a heating element coiled around the reactor to a cooling device. The bed pressure was controlled by means of a back-pressure regulator located in the outlet pipe. The composition of the outlet gas was monitored continuously by a dual channel gas micro-chromatograph Varian CP-4900, fitted with a thermal conductive detector (TCD), using helium as the carrier gas. The TCD response was calibrated using standard mixtures of CO₂ and N₂ of known composition.

Breakthrough tests were carried out at 303 K and 130 kPa for the three adsorbents. Prior to CO₂ adsorption, the adsorbent bed was initially free of CO₂ and full of N₂. Desorption was accomplished by heating the bed up to 373 K with 10 cm³ min⁻¹ (STP) of N₂ for 1 h.

A simple two-step TSA cycle was also carried out in the fixed-bed adsorption unit with samples R and A, simulating a two-columns operation with equal duration for the adsorption and desorption steps. The bed was externally cooled to 303 K during the adsorption step, and heated up to 373 K during the desorption step. Pressure was kept constant at 130 kPa. The feed flow rate used during the adsorption step was 34 cm³ min⁻¹ (STP) and the inlet concentration of CO₂ 17 vol.%. During the desorption step, the bed was purged with 2.6 cm³ min⁻¹ (STP) of N₂.

3. Results and discussion

3.1. Breakthrough curves

Figure 3a presents the CO₂ breakthrough curve of carbon C in terms of CO₂ concentration at the outlet versus time, for a feed flow rate of 36 cm³ min⁻¹ (STP) consisting of 21 vol.% CO₂ in N₂. At the beginning of the experiment, CO₂ is not detected in the effluent stream, as all the CO₂ is retained by the adsorbent bed. The
adsorption front reaches the thermocouple at around 2 min as can be observed from the small peak in the temperature profile (note that the peak is minimized due to the action of the temperature control: the bed was externally cooled to maintain a constant temperature of 303 K during adsorption). After 2.8 min, CO$_2$ is suddenly detected, indicating that the mass transfer zone has reached the bed outlet, and after 6 min the bed is fully saturated (the outlet CO$_2$ concentration reaches a constant value equal to that of the feed). Integrating the area between the ordinate axis and the curve [8], a CO$_2$ adsorption capacity of 0.47 mol/kg was obtained for carbon C under the aforementioned conditions.

Figure 3b shows the evolution of the CO$_2$ concentration at the outlet when the saturated bed is regenerated by means of heating the solids up to 373 K in 10 cm$^3$ min$^{-1}$ of N$_2$ (STP). The CO$_2$ concentration increases as the bed is heated, going through a maximum at 3 min, and rapidly decreasing thereafter (CO$_2$ < 1 vol.% for t >10 min). As can be seen from the figures, both adsorption and desorption curves are quite abrupt, which indicates reduced mass transfer resistances. In the ideal case of absence of axial dispersion and mass resistance, the breakthrough curve would be a perfect step. It must be taken into consideration that C is an activated carbon with a wide pore size distribution, including a significant amount of meso and macropores which facilitate mass transfer (feeding pores).

Figure 3a compares the CO$_2$ breakthrough curves of the commercial activated carbon, R, and the aminated biomass-based carbon, A, for a feed flow rate of 34 cm$^3$ min$^{-1}$ (STP) consisting of 17 vol.% CO$_2$ in N$_2$. Carbon R has been selected as a reference carbon because it is used commercially to reduce CO$_2$ levels in cold warehouses, and also because it showed adequate CO$_2$ capture performance in a previous study [20]. The breakthrough curves clearly show that N$_2$/CO$_2$ separation is feasible using these carbon adsorbents: during the first 8 min of the experiment (10 min in the case of A) CO$_2$ is not detected in the effluent stream. Although the breakthrough curves are slightly more dispersive than that of carbon C, the breakthrough times are still relatively fast, and the bed is fully saturated after around 15 min. The resistance to mass transfer is greater for carbons R and A when compared to C, because R and A are essentially microporous carbons [12, 18]. However, the bed still presents adequate dynamics with sufficiently low mass transfer resistances. Moreover, sample A presents a steeper curve than commercial activated carbon R.

Figure 4b shows the desorption curves for carbons R and A, obtained by heating the bed up to 373 K while purging with 10 cm$^3$ min$^{-1}$ (STP) of N$_2$. As the adsorbent bed is heated, CO$_2$ is desorbed, and the CO$_2$ concentration at the bed outlet increases, going through a maximum at 4 and 6 min for A and R, respectively. Although the vast majority of CO$_2$ has been desorbed after 30 min (CO$_2$ < 1 vol.%), CO$_2$ concentration continues to tail away after 60 min. This behavior can be explained by a favorable adsorption equilibrium, which becomes unfavorable for desorption. It must be taken into consideration that other adsorbents, such as zeolites, present much more hindered regeneration. Moreover, it can be observed from the figure that A presents a steeper desorption curve than R, showing easier regeneration than the commercial activated carbon. The bed temperature at which the maximum CO$_2$ concentration was reached follows the order: C < A < R (347, 351 and 359 K, respectively). C is an acidic carbon
with a wide pore size distribution, thus presenting weaker CO₂ adsorption forces and being easily regenerated. However, when comparing samples R and A, both essentially microporous, the presence of nitrogen functionalities in the latter should be considered. Contrary to expected, it seems that the presence of nitrogen functionalities does not hinder CO₂ desorption from carbon A. The difference in regeneration behaviour between R and A may arise from the smaller particle size of A (1-3 mm granulates versus extrudates of 3 mm diameter) which facilitates intraparticle mass transfer (kinetic effect).

Figure 4  Fixed-bed adsorption experiments for the commercial activated carbon R, and the aminated biomass-based carbon, A: a) CO₂ breakthrough curves at 303 K and 130 kPa, with a feed flowrate of 34 cm³ min⁻¹ (STP) consisting of 17 % CO₂ in N₂; b) CO₂ desorption curves obtained by heating the bed up to 373 K at 130 kPa feeding 10 cm³ min⁻¹ (STP) of N₂.

Ten consecutive breakthrough curves were obtained for samples R and A alternating the adsorption and desorption steps (1 h duration each) for 24 h (see Figure 5a). The evaluated adsorbents did not present decay in the adsorption capacity over this period of time (see Figure 5b). It is important to highlight that the CO₂ adsorption capacity of the aminated biomass-based carbon, A, is slightly above that of the commercial activated carbon, R, taken as reference, as it should be expected according to the CO₂ equilibrium data at low pressures (Figure 1). The CO₂ adsorption capacity of carbon C has not been included in the figure because the experiment was carried out in slightly different conditions (slightly higher CO₂ flow rate). Eventhough, it must be pointed out the significant lower CO₂ adsorption capacity of this carbon, when compared to those of samples R and A, in spite of its superior textural development.

Figure 5  a) Evolution of the outlet CO₂ concentration and bed temperature profile during ten consecutive breakthrough curves over R; b) CO₂ adsorption capacity of adsorbents R and A obtained from ten consecutive breakthrough curves.
3.2. TSA cycles

The consecutive breakthrough curves can be regarded as extended TSA cycles with long adsorption and desorption steps, in which the adsorbent is fully saturated at 303 K and deeply regenerated at 373 K. However, in a TSA cycle, the length of the adsorption step is usually kept below the breakthrough time, to avoid product losses in the effluent. Moreover, as it has been previously shown, although all the adsorbed CO₂ can be recovered, the CO₂ concentration in the product stream starts to decay with time: the longer the regeneration step, the higher the CO₂ recovery can be, but at the cost of a lower purity. Therefore, regeneration is usually stopped before completion, and hence the adsorption capacity of the bed reduced. The term working capacity is commonly used to refer to the effective adsorption capacity of an adsorbent bed working in continuous adsorption-desorption cycles.

A simple two-step TSA cycle with equal duration for the adsorption and regeneration steps was conducted. The step time was set to 7 and 9 min for carbons R and A respectively, according to their breakthrough curves. Figure 6 presents the 10th cycle (cyclic steady state) for the adsorbents R and A. Comparing the performance of both adsorbents, it can be seen that the effluent is more deeply decarbonized when the bed is filled with sample A. With the current cycle configuration (not optimized), CO₂ is concentrated from 17 to 43 and 59 % when testing samples R and A, respectively. Moreover, as discussed before, sample A is more readily regenerated than carbon R: the maximum CO₂ concentration during the regeneration step is attained at the end of the regeneration step for carbon R, whereas it occurs at the beginning of the step for A. This is important, as it implies that for sample A, it could be possible to obtain higher CO₂ purities by shortening the regeneration step. Due to the incomplete regeneration of the bed during the desorption step and the initial temperature of the adsorbent at the beginning of the adsorption step, the working capacities of samples R and A are limited to 0.19 and 0.46 mol kg⁻¹, respectively. Even though, the CO₂ productivity (based on total cycle time) of samples R and A keeps a value of 0.8 and 1.5 mol CO₂ kg⁻¹ adsorbent h⁻¹, respectively. Finally, it is important to highlight that no signs of deactivation were detected for carbon R after 11 consecutive cycles or for sample A after 40 cycles.

![Figure 6](image-url)

Figure 6 Evolution of the bed temperature and CO₂ concentration at the bed outlet during a TSA cycle at cyclic steady state: a) R; b) A.

4. Conclusions

The aminated biomass-based carbon presented here has shown the best CO₂ capture performance when compared to two commercial activated carbons with superior textural development. Moreover, the introduced nitrogen functionalities do not seem to hinder regeneration, as concluded from the comparison with a commercial activated carbon with similar CO₂ adsorption capacity. The biomass-based adsorbent was subjected to 40 TSA consecutive cycles with no signs of deactivation encountered. Thus, it displays promising features as adsorbent for CO₂ capture applications under post-combustion conditions.
5. Acknowledgements

This work was carried out with financial support from the Spanish MICINN (Project PSE-CO2: PS-120000-2005-2; Project ENE2008-05087). M.G.P. acknowledges support from the CSIC I3P Program co-financed by the European Social Fund.

6. References