Adsorption of CO₂ on Amine-Grafted Activated Carbon

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ABSTRACT: Adsorption on amine-grafted materials may be a potentially attractive alternative to capture CO₂ from power plants. Activated carbon (AC) has been proposed as a potential adsorbent due to its natural affinity for CO₂ and the possibility of tailoring its textural properties and surface chemistry to enhance capacity and selectivity. An AC commercial sample was functionalized with monoethanolamine to obtain nitrogen-enriched AC with two different loadings (ACN10 and ACN20). Characterization of the sample was carried out by nitrogen adsorption–desorption isotherms at 77 K, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and adsorption microcalorimetry. The CO₂ equilibrium adsorption experiments were carried out in a volumetric system within the pressure range from vacuum to 13 bar, at 298 and 348 K. Impregnated AC showed different chemical and textural characteristics with a significant reduction in the surface area, depending on the amine loading. A high adsorption capacity at room temperature (298 K) and high pressure was observed for the pristine AC as compared with the modified samples. The reduction in surface area affected the adsorption capacity of CO₂ at 298 and 348 K, except for adsorption on ACN10 at 348 K, which suggests the occurrence of chemisorption.

1. INTRODUCTION

CO₂ is the major greenhouse gas (GHG), which may cause undesired consequences to the environment, such as global warming. Although atmospheric CO₂ accounts for only 0.035% of the composition of air, it is the most abundant gas among the GHGs, which also include methane, nitrous oxide and chlorofluorocarbons (Yang et al. 2008).

The main anthropogenic source of CO₂ emission is the combustion of fossil fuels, particularly for power generation (Lee et al. 2002; Grande and Rodrigues 2008). However, there are other scenarios in which CO₂ capture is required, for example, for the purification of natural gas, biogas and syngas (Rios et al. 2011, 2013). The Intergovernmental Panel on Climate Change (IPCC) has reported that CO₂ capture systems in power plants can reduce CO₂ emissions down to 10–20% of the current values, with an efficiency of up to 85–95% (IPCC 2005). Thus, different technologies, such as absorption, membrane-based separation, adsorption and cryogenic distillation, have been studied to capture CO₂ from stationary sources (Ebner and Ritter 2009).

However, the major challenge for carbon capture and storage (CCS) technologies is the large amount of energy input required in the capture process. Approximately 70% of the total operating cost
of CCS is related to the selective capture of CO$_2$ from flue gas in power plants (Haszeldine 2009). For the separation of CO$_2$ by absorption using alkanolamines, it is well-known that most of the cost is associated with the energy input required for solvent regeneration (Idem et al. 2006). Thus, reduction in the consumption of energy during the regeneration of the capture agent is one of the most crucial requirements to improve the overall energy efficiency of CO$_2$ capture (Sumida et al. 2012).

Regarding the CCS technologies, adsorption may be an alternative separation technology depending on the successful development of tunable porous materials to capture CO$_2$ at particular conditions and release it with relatively low energy consumption (Bulánek et al. 2010). The major difficulty in capturing CO$_2$ from flue gases is the low partial pressure of CO$_2$ and fairly high temperatures involved (e.g. 348 K). Amine-modified materials are claimed to be potentially effective for the capture of CO$_2$ from flue gases owing to the smaller decrease—or even increase—in adsorption capacity at higher temperatures as compared with physisorbents (Aroua et al. 2008; Choi et al. 2009; Bezerra et al. 2011; Sumida et al. 2012).

Various adsorbents modified with amines have been investigated as potential materials for CO$_2$ capture, which include activated carbons (ACs), zeolites, mesoporous silicas, clays and metal-organic frameworks (Chatti et al. 2009; Dantas et al. 2010; Bezerra et al. 2011; Khalil et al. 2012; Sumida et al. 2012; Kim et al. 2013). In this context, AC has been proposed as a potential support adsorbent due to its affinity for CO$_2$ and the possibility of tailoring its textural properties and surface chemistry. Khalil et al. (2012) studied the adsorption of CO$_2$ from a gas mixture stream on AC particles modified with monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol. Although the impregnation process led to pore filling and subsequent reduction in surface area, there was an enhancement on adsorption capacity and selectivity for CO$_2$. However, this is not a general rule, because there are other studies which show that grafting of amine groups on AC has been accompanied by a decrease in CO$_2$ adsorption capacity at several temperatures (Dantas et al. 2010). In fact, it seems there is an optimal concentration at which there is a compromise between the decrease in surface area available for physisorption and the generation of amine-active sites that will bind CO$_2$ selectively at a wider temperature range.

In this study, nitrogen functional groups were introduced on commercial AC by impregnation of a primary amine in an attempt to enhance the adsorbed concentration of CO$_2$ at high temperatures (e.g. 348 K). Commercial AC was impregnated by immersing it in MEA solutions under different amine concentrations (0–20% vol/vol). To evaluate the textural, structural and surface modifications induced by the impregnation process, the resulting adsorbents were characterized by a variety of analytical techniques such as nitrogen adsorption–desorption isotherms at 77 K, thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and CO$_2$ adsorption microcalorimetry. The potential use of these materials as CO$_2$ adsorbents was investigated at two temperatures (298 and 348 K) and within the pressure range from vacuum to 13 bar using a gravimetric device.

2. EXPERIMENTAL ANALYSIS
2.1. Materials

MEA (99.9%, VETEC, Duque de Caxias, Brazil) and methanol (99.9%, VETEC) were used as obtained from the manufacturer. The gases used in the experiments (CO$_2$ and He) were supplied by White Martins with purity of 99.995% for He and 99.8% for CO$_2$. The commercial AC was
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provided by MeadWestvaco (Richmond, VA). The AC was washed with deionized water to remove fine particles and then dried in an oven at 373 K for 24 hours.

2.2. Impregnation Process of AC

Impregnated AC was prepared by immersing the sample (2 g) in a methanolic solution of MEA (50 ml) and placing the suspension inside a rotary evaporator system (VETEC). The system was maintained at a constant temperature of 323 K (close to the boiling point of the solvent) and vacuum. The impregnation process was conducted with a moderate rotation until complete evaporation of the solvent. The sample was then dried at 423 K under an inert atmosphere (nitrogen flow). Two amine concentrations (10% and 20% vol. in methanol) were studied and the thus prepared samples were denoted as ACN10 and ACN20.

2.3. Characterization Methods

Nitrogen adsorption–desorption isotherms at 77 K were measured in an automated manometric system ASAP 2000 (Micromeritics Instrument Corporation) to determine textural characteristics of the samples. Before performing the measurements, the samples were outgassed at 373 K and under vacuum ($10^{-5}$ bar). Adsorption data were used to calculate BET surface area ($S_{BET}$) and total pore volume ($V_{TOTAL}$). XPS data were collected on a Physical Electronics spectrometer (Model 5700) under ultrahigh vacuum ($10^{-9}$ bar). The surface functional groups were investigated by FTIR using a Perkin-Elmer spectrometer. The samples were diluted with KBr at a mass ratio (KBr: sample) equal to 20:1 to improve their reflectivity. A spectrum of pure KBr was recorded as background.

The CO$_2$ adsorption microcalorimetry experiments were performed at 273 K and up to 101 kPa, using a Tian–Calvet-type isothermal microcalorimeter coupled with a home-made manometric dosing apparatus (Silva et al. 2012). This microcalorimeter consists of two thermopiles with several thermocouples mounted in electrical opposition. Thus, this system allowed us to obtain adsorption isotherms and differential enthalpies as a function of the gas coverage.

2.4. CO$_2$ Adsorption Measurements

Before performing adsorption experiments, the samples were degassed for 12 hours under vacuum at 373 K. The CO$_2$ adsorption isotherms were measured at 298 and 348 K in the pressure range of 0–13 bar using a gravimetric device (magnetic suspension balance by Rubotherm, Bochum, Germany).

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization

3.1.1. Nitrogen Adsorption–Desorption Isotherms

The influence of the amine impregnation on the textural characteristics of the samples was investigated by analyzing the nitrogen adsorption and desorption isotherms at 77 K. The nitrogen isotherms of the sorbents are shown in Figure 1. All the isotherms were classified as Type I in accordance with the IUPAC classification with characteristic predominance of micropores, although the pristine AC has a rather smooth knee,
which is indicative of the presence of mesopores. A high volume of nitrogen was adsorbed in the relative pressure range of 0–0.2, and thus it can be concluded that all adsorbents are predominantly microporous. There was a small hysteresis loop on nitrogen isotherms for all the samples in the relative pressure range of 0.4–0.8, which is associated with capillary condensation of nitrogen in slit-like mesopores.

According to Khalil et al. (2012) there were many empty pores available in the pristine sample, which could be used to absorb nitrogen molecules (on nitrogen adsorption–desorption isotherms analysis). However, for ACN10 and ACN20, the pores were blocked by amines, which may sterically hinder the diffusion of nitrogen molecules. In fact, the diffusion resistance and intra-particle mass transfer of nitrogen through filled pores may prevent the achievement of a strict equilibrium in the adsorption branch (Olea et al. 2013), especially at 77 K. Note that, in this study, the surface area was not as drastically affected (Table 1) as in other studies, which report reductions in the surface area down to some tenths of m²/g (Khalil et al. 2012; Houshmand et al. 2013; Lee et al. 2013). However, from another point of view, the surface area decrease can also demonstrate that amines were successfully incorporated to the surface of adsorbent.

Finally, the pore-size distribution (PSD) of the materials was determined using the non-linear density functional theory method from the nitrogen isotherms at 77 K. In Figure 2, it can be seen that the carbon matrix has a wide range of PSD with a major fraction in the range of micropores (<20 Å).

**TABLE 1.** Textural Characteristics of the Investigated Adsorbents

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{BET}) (m²/g)</th>
<th>(V_{TOTAL}) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1727</td>
<td>1.204</td>
</tr>
<tr>
<td>ACN10</td>
<td>749</td>
<td>0.468</td>
</tr>
<tr>
<td>ACN20</td>
<td>237</td>
<td>0.175</td>
</tr>
</tbody>
</table>

![Figure 1. Nitrogen adsorption isotherms at 77 K of the studied samples.](image-url)
After modification by MEA, a reduction of the pores in the microporous range confirms that the MEA was loaded into the micropores and a higher concentration of MEA solution entails a higher reduction in the range of micropores. Furthermore, it is noted that the AC PSD starts at 5 Å, whereas the PSD of the amine-modified materials begins from 9 Å. This confirms the filling of most of the micropore fraction by MEA.

### 3.1.2. XPS Analysis

The XPS measurements were performed to investigate the interaction between MEA and the surface of AC. The nitrogen functional groups were measured by XPS and could be identified by examining the C 1s, O 1s and N 1s core regions. Atomic concentrations and binding energies obtained from XPS are shown in Table 2. As expected, the XPS spectra indicate that the unmodified AC sample contained only C and O elements and after MEA modification, a new XPS peak appears at 400.5 eV, suggesting the presence of nitrogen in the samples.
The main C 1s peak was deconvoluted into four peaks centred on the binding energies of 284.8, 286.4, 288.6 and 290.7 eV corresponding to the bonds C–C, C–N, C–O and π–π*, respectively (Yu et al. 2012; Guo et al. 2013). The percent areas under the peaks reflect the relative concentration of each bond. This reveals that AC contains more C–C and π–π* bonds than the impregnated samples ACN10 and ACN20, whereas the latter samples exhibit a higher concentration of C–N bonds. This is an indication that there are amino groups attached to the carbon surface due to the impregnation. The peak 288.6 eV (C–O) presented a slight increase in the two samples (ACN10 and ACN20) attributed to the presence of one oxygen molecule in the amine.

3.1.3. FTIR Analysis

To determine whether new functional groups have been attached to AC surface after impregnation, FTIR analysis was used. Figure 3 shows the FTIR spectra for the pristine sample (AC) and that impregnated with the highest amine loading (ACN20) over the wave number range of 3600–600 cm\(^{-1}\).

The results showed that the AC has surface functionalities related to oxygenated groups: a peak between 1700 and 1682 cm\(^{-1}\), which could be assigned to the C–O groups on the surface of the carbon (lactonic, ether, phenol, etc.), and another peak at 1700–1682 cm\(^{-1}\), which could be attributed to C=O (carboxylic, anhydride, lactone and ketone groups; Tomaszewski et al. 2003). For the amine-grafted carbon, the main difference observed was the appearance of two broad peaks at 1620 to 1610 cm\(^{-1}\) and at 1375 to 1175 cm\(^{-1}\), which are indicative of the presence of N–H in the surface material (Yu et al. 2012; Lin et al. 2013) and C–O–C, as a result of possible dehydration reaction between two hydroxyl groups (one belonging to the amine with another from the AC) taking place in amine grafting. For both samples, a peak between 2380 and 2270 cm\(^{-1}\) is observed, which is associated with the asymmetric stretching vibration of the gas-phase O=C=O, that is, physisorbed CO\(_2\) from the air (Caglayan and Aksoylu 2013). Such a peak is significantly

![Figure 3. FTIR spectra for AC sample and the amine-loaded sample (ACN20).](image-url)
more intense in the amine-loaded sample, which suggests a stronger interaction of the surface with CO₂ brought about by the incorporation of MEA.

### 3.2. Adsorption Isotherms

Adsorption isotherms of CO₂ on AC (pristine sample) measured at pressures up to 10 bar and at two different temperatures (298 and 348 K) are shown in Figure 4.

The adsorption capacity of small molecules such as gases depends on the amount of micropores of a specific diameter and volumes as well as on the chemical surface characteristics of sorbents (Lin et al. 2013). The superior textural properties of the pristine sample (AC) resulted in high adsorption capacity values, mainly at 298 K (indicating a predominantly exothermic process). The AC sample presented an increase in the adsorption capacity for all the pressure range studied. This is a consequence of the textural properties, which reveal a wide range of PSD (microporous and mesoporous) observed in Figure 1.

The CO₂ adsorption isotherm on the ACN20 sample is shown in Figure 5 under similar experimental conditions.

The CO₂ adsorption capacity of the amine-loaded AC (ACN20) was lower than that of the pristine AC, which may be explained by the fact that the surface area and porous volume of sorbents were reduced due to amine impregnation, as shown in Table 2. The pore filling of AC with amine was inappropriate and possibly led to obstruction/destructions of a considerable number of physisorption sites. Therefore, the resulting material presented low CO₂ uptake, in accordance with its low surface area, 237 m²/g.

The great difficulty in using functionalized sorbents with small pores is an adequate filling with the target functionalization moiety. The concentration of the impregnating solution and the experimental procedure are important factors that may lead to an adsorbent, which will bind CO₂ predominantly either by physisorption or chemisorption. To apply such materials for CO₂ adsorption of CO₂ on Amine-Grafted Activated Carbon
adsorption from flue gases, a sorbent with both physical and chemical adsorption properties is desirable, particularly because of the temperature range of such emissions (323–353 K).

In the search of an absorbent with a balance of such properties, the sample ACN10, with an intermediate amine load, was analyzed. The adsorption data at 298 and 348 K are shown in Figure 6. In this case, experimental results indicate that CO₂ adsorption capacity is not only determined by the BET surface area, but also by the surface properties, especially the basic functional groups. The adsorption capacity results were calculated in units of mmol/g and mmol/m² at given pressures and are summarized in Table 3.

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**Figure 5.** Adsorption isotherms CO₂ in ACN20 at 298 and 348 K.

**Figure 6.** Adsorption isotherms of CO₂ in ACN10 at 298 and 348 K.
The adsorption of CO₂ for the pristine sample was essentially due to physisorption, and hence depended only on the surface area and pore volume available in the adsorbent. The sample AC has the largest surface area, 1727 m²/g, and the highest physisorption capacity at low temperature, over 6 mmol CO₂/g at 10 bar.

Samples ACN10 and ACN20 presented a decrease in the adsorption capacity at low temperature, 298 K, as a result of the detrimental effect of amine impregnation on the textural properties. According to a previous study in this group (Bezerra et al. 2011), at low temperatures, this effect may be attributed to either size exclusion or diffusion limitations imposed by the pore blocking with amine. Nonetheless, sample ACN10 presented a different behaviour at high temperature (i.e. 348 K). Its adsorption capacity (on mmol/g and mmol/m²) was superior than the pristine sample. Such behaviour may be due to a temperature-controlled reaction, that is, favoured in high temperature (chemisorption). This also is consistent with the diffusion effects, that is, at high temperatures, intra-particle mass transfer is possibly enhanced. It is likely that both mechanisms (chemisorption and resistance diffusion) occur.

Also note that, in mmol/m², nearly all samples have the same CO₂ adsorption capacity at 298 K, which is another evidence that physisorption is the main mechanism in such a temperature. At higher temperatures, ACN10 seems to have a balanced amount of loaded amine, which successfully enhanced adsorption capacity despite the much lower surface area as compared with the pristine sample.

The CO₂ adsorption calorimetric experiments were carried to further investigate the hypothesis of chemisorption in the sample AC and ACN10. In Figures 7 and 8, the adsorption isotherms and calorimetric curves of the two samples at 273 K are shown.

From the volumetric–calorimetric isotherms (Figure 7), it can be seen that MEA loading has decreased CO₂ adsorption capacity compared with unmodified carbon, as previously observed in isotherms measured at other temperatures. From differential adsorption enthalpy measurements (Figure 8), it is observed that the curves of the adsorption enthalpies for AC and ACN10 are relatively similar, except for the first measured point, which is notably higher for the amine-loaded sample (−38 kJ/mol for AC and −47 kJ/mol for ACN10). This behaviour suggests that chemisorption is not significant in CO₂ adsorption at 273 K (except for very low coverage) and thus, the physisorption is the dominant mechanism. As the temperature increases, the role of chemisorption in the amine-loaded sample ACN10 becomes more evident, as can be observed in the values shown in Table 3, particularly on a mmol/m² basis.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>ACN10</th>
<th>ACN20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K</td>
<td>0.131</td>
<td>0.045</td>
</tr>
<tr>
<td>1 K</td>
<td>1.202</td>
<td>0.430</td>
</tr>
<tr>
<td>10 K</td>
<td>6.571</td>
<td>2.926</td>
</tr>
<tr>
<td>0.1 K</td>
<td>0.696</td>
<td>0.250</td>
</tr>
<tr>
<td>1 K</td>
<td>3.80</td>
<td>1.694</td>
</tr>
<tr>
<td>10 K</td>
<td>0.877</td>
<td>4.101</td>
</tr>
<tr>
<td>1 K</td>
<td>4.909</td>
<td>4.498</td>
</tr>
<tr>
<td>10 K</td>
<td>0.984</td>
<td>1.477</td>
</tr>
</tbody>
</table>
Figure 7. CO$_2$ adsorption isotherms at 273 K by joint volumetry–calorimetry.

Figure 8. Differential enthalpies of CO$_2$ adsorption at 273 K.

4. CONCLUSION

Two modified AC samples were obtained by loading the pristine sample (AC) with MEA by wet impregnation (ACN10 and ACN20). It has been shown that MEA tends to fill and eventually block the pores of the adsorbent. The XPS and FTIR analyses reveal that nitrogen is covalently attached to the adsorbent surface. At low temperatures (room temperature and below), physisorption in the main bonding mechanism of CO$_2$, regardless of the amine concentration loaded to the adsorbent. At higher temperatures, though, the presence of amine in moderate amounts seems to enhance CO$_2$ uptake by a synergistic combination of physisorption and chemisorption. As a result, ACN10 adsorbs more CO$_2$ than the pristine material as temperature rises, unlike ACN20. For the latter, loaded amine was excessive and led to such a detrimental
effect on the textural properties that the expected increase in uptake by chemisorption at higher temperature could not be observed.

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