

# CO<sub>2</sub> ADSORPTION FROM SIMULATED FLUE-GAS ON ACTIVATED CARBON MONOLITHS

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## Abstract

This work deals with the adsorption of CO<sub>2</sub> on activated carbon (AC) monoliths in a lab-scale fixed-bed reactor from simulated flue-gas. Tests were carried out at different temperatures (303 and 353 K) and for a 15% CO<sub>2</sub> concentration (typical of flue-gas). The textural characterization of the monolith samples was carried out by N<sub>2</sub> adsorption at 77 K, while Boehm titration analysis and pH<sub>PZC</sub> determination were used for a chemical characterization of the samples.

The adsorption tests show a maximum CO<sub>2</sub> adsorption capacity for the sample with the greatest ultramicropore volume, while the adsorption rate increases in presence of mesopores and for higher temperature. Moreover, dedicated regeneration studies demonstrate that the monolith samples can be fully regenerated at each investigated adsorption temperature and the CO<sub>2</sub> adsorption capacity keeps almost constant in five consecutive cycles of adsorption-desorption.

## Introduction

The increase in CO<sub>2</sub> emissions, mainly by the combustion of fossil fuels such as coal, oil and natural gas, plays a major role in the alteration of the energy balance of the Earth, leading to a global climate change. For this reason, new and more efficient CO<sub>2</sub> capture techniques must be put forward. In this scenario, adsorption represents an attractive purification technology, widely used for the treatment of gaseous and liquid effluents due to its high operating flexibility, general low maintenance costs and, if coupled with an effective regeneration process, for the absence of by-products [1, 2]. For CO<sub>2</sub> capture applications, many sorbents can be used either raw or functionalized. Activated carbon (AC) is one of the most attractive materials thanks to its high surface area, highly developed porous structure and its ability to exhibit different texture and chemical properties [3].

AC are typically obtained either in a finely powdered form or as granular material to make them suitable for handling in different devices. However, in spite of the widespread utilization of granular/powdered adsorbents, there are some drawbacks when applied to real-scale, such as high pressure drop, channeling, gas bypassing in packed beds, attrition due to the granular material and to particle entrainment in

fluidized beds [4]. As an alternative to overcome these drawbacks, the production of AC monoliths is gaining crescent interest, also for CO<sub>2</sub> capture.

Moreover, appropriate post-synthesis surface modifications can be an interesting tool to further improve the adsorbent performances; for CO<sub>2</sub> capture, several studies have established that incorporating nitrogen groups increases the selectivity of the surface of the carbonaceous materials for this molecule [5].

This work aims at investigating the use of AC monoliths for CO<sub>2</sub> adsorption applications. To this aim, two samples were synthesized starting from a same lignocellulosic precursor – an African palm stone (*Elaeis guineensis*) - by two different activating aqueous solutions. Subsequently, the monolith samples were functionalized with a 30% ammonium hydroxide aqueous solution.

The monolith samples were characterized in terms of pore structure by adsorption of nitrogen at 77 K and chemical surface properties by Boehm titration analysis and pH<sub>PZC</sub> evaluation. CO<sub>2</sub> adsorption tests from simulated flue-gas were carried out in a lab-scale plant based on a fixed-bed column, at two temperature levels (i.e. 303 and 353 K). Finally, the regeneration of one of the AC monoliths and the reutilization within consecutive cycles of adsorption-desorption were assessed.

### **Materials and Methods**

AC monoliths were prepared using African Palm stones as lignocellulosic precursor. The activation process was conducted in aqueous solution of either H<sub>3</sub>PO<sub>4</sub> 48% w/v (MP48 sample) or a combination of H<sub>3</sub>PO<sub>4</sub> (32% w/v) + CaCl<sub>2</sub> (2% w/v) (MCA2 sample). The monoliths were prepared using a compacting process, which determined an outer diameter of 1.5×10<sup>-2</sup> m, a height of 8×10<sup>-3</sup> m, and six parallel internal channels, each with an inner diameter of 3×10<sup>-3</sup> m. A subsequent carbonization process was carried out in order to further develop the porosity of the adsorbents. After the synthesis, the MP48 and MCA2 samples were subjected to a same functionalization process, conducted in aqueous phase with a 30% w/w ammonium hydroxide solution.

The textural properties of all the synthesized monoliths were analyzed using N<sub>2</sub> adsorption measurements at 77 K in a volumetric system (Quantachrome, Autosorb 3-B). The content of surface functional groups of the AC monoliths was determined by Boehm titrations, while the determination of the point of zero charge (pH<sub>PZC</sub>) for all the synthesized monoliths was performed by means of mass titration method.

The CO<sub>2</sub> adsorption runs were carried out in a lab-scale fixed-bed column (length=0.13 m; inner diameter=0.015 m) made up of Pyrex glass, at two different levels of temperature i.e. 303 and 353 K and 15% CO<sub>2</sub> concentration.

Experimental tests were carried out by feeding the column with a 2.5×10<sup>-2</sup> L s<sup>-1</sup> gas stream (15% CO<sub>2</sub>, balance N<sub>2</sub>) at 1 atm. A fixed adsorbent amount (i.e. 10 g, corresponding to 12 monoliths, aligned in the column along the internal channels) was used for each test.

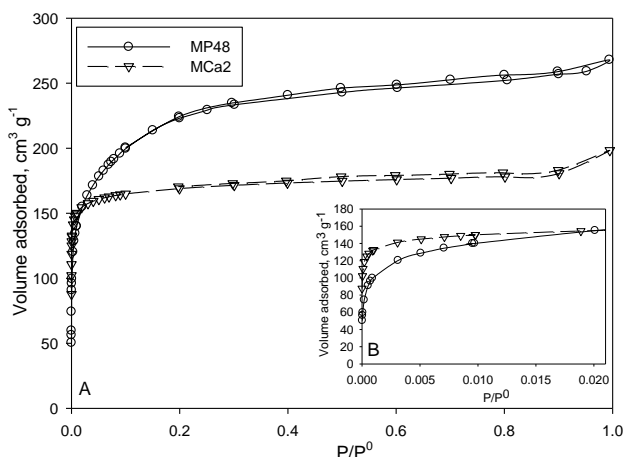
Further tests were conducted to assess the regenerability of the monoliths. After the

adsorption run at 15% CO<sub>2</sub> concentration and under the same conditions of adsorption runs, CO<sub>2</sub> desorption were carried out by fluxing pure N<sub>2</sub> as desorbing agent. The adsorption-desorption sequence was repeated for 5 consecutive cycles on the same monolith sample, keeping a constant adsorption temperature of 303 K or 353 K.

A continuous NDIR (non-dispersive infrared) gas analyzer (AO2020 Uras 26 model provided by ABB) was adopted for the determination of CO<sub>2</sub> concentration. Further details about dynamic experimental apparatus and adsorption tests are reported in a previous work [6].

## Results and Discussion

The pore structure of the AC monoliths, as derived from N<sub>2</sub> adsorption experiments, is reported in Fig. 1.



**Figure 1.** N<sub>2</sub> adsorption isotherms (T=77 K) of AC monoliths on entire P/P<sup>0</sup> range (A) and for P/P<sup>0</sup><0.02 (B)

For both the AC samples, the N<sub>2</sub> adsorption isotherms are type I according to the IUPAC classification, indicative of highly microporous materials. Both the AC monoliths are characterized by an elbow at low relative pressure (P/P<sup>0</sup><0.1), much more closed for the MCA2 sample, testifying a narrower micropore size distribution shifted towards ultramicropores. Conversely, the MP48 sample is characterized by an opening of the knee at low relative pressure, which indicates the occurrence of wider micropores. These results are much more evident if the N<sub>2</sub> adsorption data for P/P<sup>0</sup><0.02 are observed (Fig. 1B). Moreover, the MP48 has a higher contribution of mesopores that, in conjunction with a larger average pore diameter, is expected to determine a positive influence on the kinetics of CO<sub>2</sub> adsorption [6], as reported in the following.

The N<sub>2</sub> adsorption data were processed to determine the main textural parameters of the two monolith samples (Table 1).

**Table 1.** Textural parameters of AC monoliths as obtained from the N<sub>2</sub> adsorption isotherm at 77 K.

N <sub>2</sub> adsorption data at 77 K				
Sample	S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	V <sub>0</sub> / cm <sup>3</sup> g <sup>-1</sup>	V <sub>meso</sub> / cm <sup>3</sup> g <sup>-1</sup>	V <sub>t</sub> / cm <sup>3</sup> g <sup>-1</sup>
MP48	785	0.28	0.13	0.41
MCA2	658	0.26	0.05	0.31

The volume of micropores, V<sub>0</sub>, was obtained by application of the Dubinin-Radushkevich equation to the N<sub>2</sub> adsorption data. The total pore volume, V<sub>t</sub>, was obtained from the N<sub>2</sub> amount adsorbed at a relative pressure P/P<sup>0</sup> of 0.99 while the mesopore volume, V<sub>meso</sub>, was obtained from the difference between the total pore volume and the micropore volume.

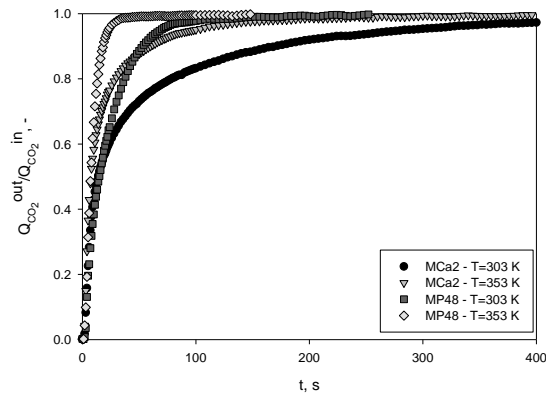
As expected, the MCA2 sample shows a lower total pore (V<sub>t</sub>) and mesopore (V<sub>meso</sub>) volume, while the differences in micropore volumes are very small.

The chemical characterization of the two AC monoliths allowed determining a higher pH<sub>PZC</sub> for the MCA2 sample (6.9 vs 6.4), a lower contribution of total acidic functional groups (133 μmol g<sup>-1</sup> vs 218 μmol g<sup>-1</sup>), mainly represented by the phenolic, and a slightly higher contribution of total basic functional groups (174 μmol g<sup>-1</sup> vs 168 μmol g<sup>-1</sup>). Evidently, all the physical and chemical properties can be ascribed to the different ability of the activating agents in determining a porous structure in the precursor. In particular, the functionalization agent provides a significant contribution to the total basicity of the samples, mainly by reaction of carboxylic groups with ammonia.

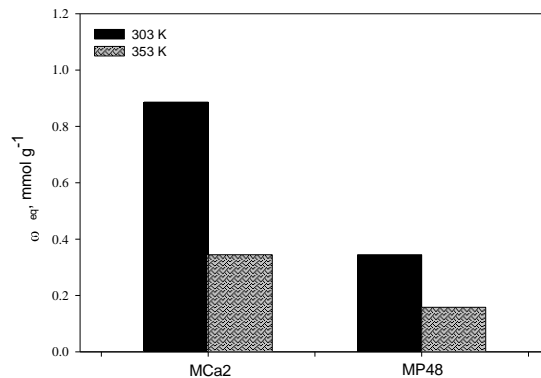
In Fig. 2, the breakthrough curves of the two AC monoliths are reported at two levels of temperature (303 and 353 K) and for a 15% CO<sub>2</sub> (balance N<sub>2</sub>).

For both the samples, an increase in temperature determines a significantly sharper slope of the breakthrough curves and a simultaneous decrease of the breakpoint time. For both the investigated temperatures, the MCA2 sample has a significantly slower capture kinetics with respect to MP48, presumably due to the simultaneous lower mesopore volume and narrower micropore contribution shifted towards ultramicropores.

The CO<sub>2</sub> dynamic adsorption data were processed to obtain the corresponding equilibrium CO<sub>2</sub> amount adsorbed on solid (ω<sub>eq</sub>, mmol g<sup>-1</sup>), through a material balance on CO<sub>2</sub> over the entire fixed-bed column. In Fig. 3, the CO<sub>2</sub> adsorption capacity of both the AC monoliths, in correspondence of a 15% CO<sub>2</sub> concentration, are reported, for the two tested temperature levels.



**Figure 2.** CO<sub>2</sub> breakthrough curves of MP48 and MCa2 samples as a function of temperature (303 K and 353 K). CO<sub>2</sub> 15% by vol, P=1 bar.

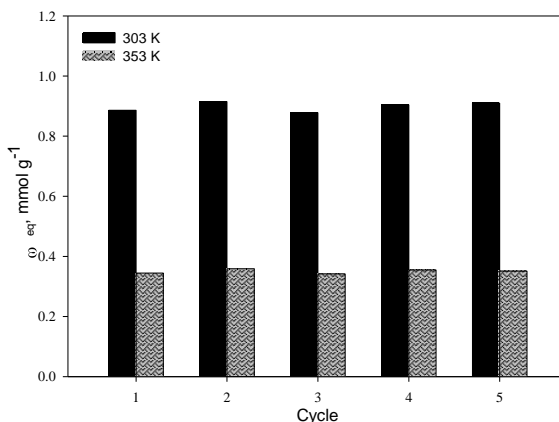


**Figure 3.** CO<sub>2</sub> adsorption capacity of MP48 and MCa2 samples as a function of temperature (303 K and 353 K). CO<sub>2</sub> 15% by vol, P=1 bar.

It can be observed that the MCa2 sample shows the largely highest CO<sub>2</sub> adsorption capacity, in particular at 303 K. Once more, this result is likely due to its porous structure, in which the narrow micropores prevail, and to its more basic surface. At 353 K, the higher basicity of MCa2 determines better performances, even if the expected exothermic effect remarkably affects the CO<sub>2</sub> adsorption capacity of both the samples.

Finally, in Fig. 4 the CO<sub>2</sub> adsorption capacity ( $\omega_{eq}$ ) of MCa2 is reported over five consecutive adsorption-desorption cycles, at different adsorption temperatures (303 K and 353 K) and for a 15% CO<sub>2</sub> gas stream.

The experimental results clearly indicates that, for both the temperatures, the MCa2 monolith can be fully regenerated and its  $\omega_{eq}$  at 15% CO<sub>2</sub> concentration keeps practically constant upon the number of cycles.



**Figure 4.** CO<sub>2</sub> adsorption capacity of MCA2 sample over 5 adsorption/desorption cycles at 303 and 353 K (CO<sub>2</sub> inlet concentration: 15% by vol.)

## Conclusions

CO<sub>2</sub> adsorption tests were carried out on two activated carbon monoliths. Experimental results indicated that the occurrence of a significant fraction of narrow micropores for MCA2 enhances its CO<sub>2</sub> adsorption capacity, while the higher mesopore volume of MP48 determines higher adsorption rate. For both the AC monoliths, an increase in the temperature determines greater adsorption rate but lower adsorption capacity.

Finally, the regenerability of the MCA2 sample and its reutilization within five consecutive cycles of adsorption-desorption was assessed, so to define the complete potentiality of its use for post-combustion CO<sub>2</sub> capture

## References

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