

# CO<sub>2</sub> ADSORPTION BY SURFACE MODIFIED CARBON SORBENTS

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## Introduction

Anthropogenic emissions have increased the CO<sub>2</sub> concentration on the atmosphere with over 30% compared to pre-industrialize levels [1]. Most of these anthropogenic emissions are caused by fossil fuel utilization, where around one-third is due to electricity generation from fossil fuel combustion, mainly from coal-fired units. Furthermore, fossil fuel electricity generation units rank as the first target to reduce anthropogenic emissions due to their stationary nature. However, the costs of current CO<sub>2</sub> separation and capture technologies are estimated to be about 75% of the total cost of ocean or geological sequestration, including the costs for compression to the required pressure for subsequent sequestration [2]. New solid-based sorbents are being investigated, where the amine groups are bonded to a solid surface, resulting in an easier regeneration step [3-5]. The supports used thus far, including commercial molecular sieves and activated carbons, are very expensive and hinder the economical viability of the process. Accordingly, there is a need to find low-cost precursors that can compete with the expensive commercial supports, and develop effective solid sorbents that can be easily regenerated, and therefore, have an overall lower cost over their lifetime performance.

Previous studies conducted by the authors have shown that high surface area activated carbon (AC) can be produced from anthracite by one-step steam activation [6], and from high carbon content chars [7-8]. These activated materials have been tested for CO<sub>2</sub> adsorption [6, 9]. However, the CO<sub>2</sub> capture capacity of activated anthracites is lower than that of commercial AC or molecular sieves [10]. Therefore, in this study, several surface treatment methods were used to modify the surface properties of the carbon sorbents to improve their CO<sub>2</sub> capture capacity.

## Experimental

### **AC samples**

The carbon sorbents used in this work include AC-PSOC1, AC-PSOC2, CC1, CC1-DEM, AC-FA1, AC-FA1-N1 and FA1-DEM. Table 1 presents the conditions used to produce these samples.

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Table 1. Conditions used to produce the carbon sorbents

Name	Feedstock	Activation temperature (°C)	Activation time (hr)	Treatment before activation
AC-PSOC1	Anthracite	850	3	-
AC-PSOC2	Anthracite	890	3	-
CC1	Fly ash	-	-	-
CC1-DEM	Gasifier char	-	-	HCl/HNO <sub>3</sub> /HF at 65°C for 4hrs
AC-FA1	Boiler char	850	1	-
AC-FA1-N1	Boiler char	850	1	(1) HCl/HNO <sub>3</sub> /HF at 65°C for 4hrs (2) 5N HNO <sub>3</sub> at boiling for 1hr
FA1-DEM	Boiler char	-	-	HCl/HNO <sub>3</sub> /HF at 65°C for 4hrs

### **Surface treatment**

(1) *NH<sub>3</sub> treatment*: A known amount of sample AC-PSOC1 was put into a quartz boat, which was placed in the middle of a horizontal tube furnace. NH<sub>3</sub> gas was then introduced, while the furnace was heated up to desired treatment temperature. After the furnace was held at the set temperature for 90 minutes, the NH<sub>3</sub> gas was switched to argon while the furnace cooled down. The sample was removed from the reactor tube at room temperature and labeled as AC-PSOC1-NH<sub>3</sub>-xxx, where the last three digits represent the treatment temperature.

(2) *Amine impregnation*: All the carbon sorbent samples were impregnated with a PEI (polyethylenimine) methanol solution and then dried in a vacuum oven at 75°C overnight. The resultant samples were labeled as PEI-x, where x represents the carbon sorbent name.

### **ACs characterization and CO<sub>2</sub> adsorption**

N<sub>2</sub> adsorption isotherms at 77K were used to characterize the porosity of the samples with a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The pore sizes 2nm and 50nm were taken as the limits between micro- and mesopores and meso- and macropores, respectively, following the IUPAC nomenclature [11]. The CO<sub>2</sub> adsorption capacity of the samples was characterized using a PE-TGA 7 thermogravimetric analyzer, as described elsewhere [6].

## **Results and Discussion**

### **Pore structure change of the sorbents after surface treatment**

The porous texture properties, as determined from the 77K N<sub>2</sub>-isotherms, of the parent activated carbons and their counterparts treated with NH<sub>3</sub> are shown in Table 2. The NH<sub>3</sub> treatment increased the surface area of the activated samples, especially at lower

temperatures (650°C), while the HNO<sub>3</sub> treatment decreased the surface area of the activated anthracites. For example, the surface area of the NH<sub>3</sub> treated activated anthracites increased from 928 to 1052 and 952 m<sup>2</sup>/g at 650 and 800°C, respectively. Most of the pores of the activated anthracites AC1 and AC2, which were produced by steam activation at 850°C using different activation times, are mainly micropores (>92%). The low temperature NH<sub>3</sub> treatment (650°C) can increase the surface area while keeping the sample microporosity (92%). In contrast, the high temperature NH<sub>3</sub> treatment (800°C) increases slightly the surface area of the anthracite, but increases significantly its pore diameter from 1.91 to 1.97 nm.

Table 2. Porous texture of the parent activated anthracites and their counterparts treated with NH<sub>3</sub>

Sample	BET surface area, m <sup>2</sup> /g	Pore volume, ml/g	Microporosity ratio, %	Average pore diam., nm
AC-PSOC1	928	0.442	92	1.91
AC-PSOC1-NH <sub>3</sub> -650	1052	0.523	92	1.91
AC-PSOC1-NH <sub>3</sub> -800	952	0.469	88	1.97

Table 3 shows the surface area and pore volume of the samples before and after PEI treatment. The surface area and pore volume of the all samples were dramatically reduced comparing to the samples before treatment. This indicates that the PEI impregnation has blocked most of the pores in the carbon sorbents.

Table 3. Porosity parameters of PEI modified samples

Sample name	Before treatment		After treatment	
	Surface area m <sup>2</sup> /g	Pore volume mL/g	Surface area m <sup>2</sup> /g	Pore volume mL/g
AC-PSOC1	928	0.442		
AC-PSOC2	639	0.351		
CC1	284	0.277	0.2	0.001
CC2-DEM	731	0.740	21.1	0.062
AC-FA1	387	0.213	1.6	0.003
AC-FA1-N1	1139	0.615	3.9	0.010
FA1-DEM	53	0.040	0.9	0.001

### **CO<sub>2</sub> adsorption studies**

The CO<sub>2</sub> adsorption capacities of the activated anthracites and their NH<sub>3</sub> treated counterparts were determined at 30, 50 and 75°C, as shown in Figure 1. It can be seen that there are significant changes in the CO<sub>2</sub> adsorption capacity of the parent and treated anthracites with temperature. At 30°C, the adsorption of the untreated activated anthracites was slightly higher than the treated samples. At higher adsorption temperatures (50°C and 75°C), the adsorption of the treated samples was slightly higher than the parent activated anthracite. For instance, at 75°C, the CO<sub>2</sub>

adsorption capacity was 21.68, 26.63 and 23.69 mg-CO<sub>2</sub>/g-sorbent for AC-PSOC1, AC-PSOC1-NH<sub>3</sub>-650 and AC-PSOC1-NH<sub>3</sub>-800, respectively.

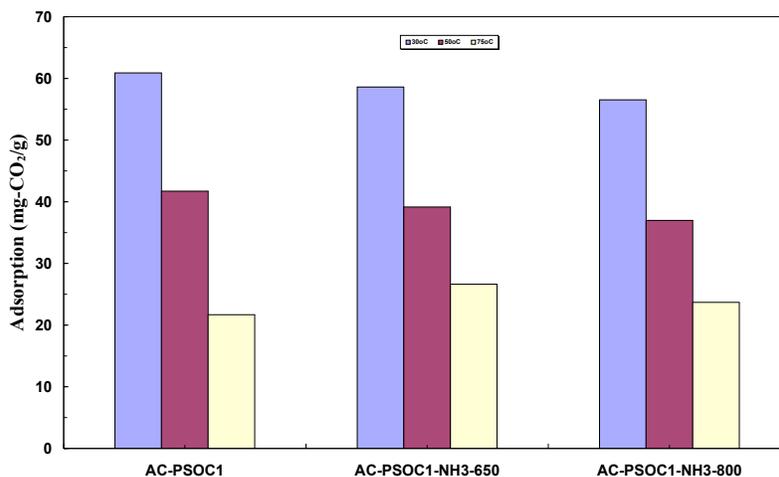


Figure 1. CO<sub>2</sub> adsorption capacities of AC-PSOC1 and its NH<sub>3</sub> treated samples, AC-PSOC1-NH<sub>3</sub>-650 and AC-PSOC1-NH<sub>3</sub>-800

Figure 2 shows the CO<sub>2</sub> adsorption capacities at 75°C of the all carbon sorbents, and their PEI impregnated samples. It can be seen that impregnation with PEI increases significantly the CO<sub>2</sub> adsorption capacities of all the samples. For instance, the adsorption capacity increased from 16.94 to 37.49 mg-CO<sub>2</sub>/g for AC-PSOC2 after impregnation, and it increased from 21.99 to 93.64 mg-CO<sub>2</sub>/g for CC1-DEM sample.

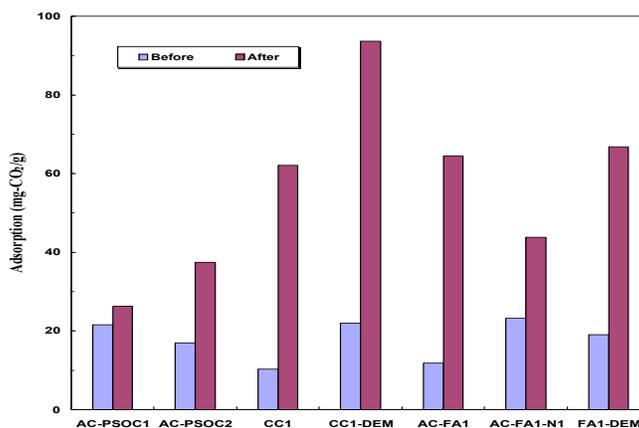


Figure 2. CO<sub>2</sub> adsorption capacities at 75°C of all carbon sorbents and their PEI impregnated samples

The increased CO<sub>2</sub> capacity after amine impregnation is consistent with that found in molecular sieve materials MCM-41 [5]. The carbon sorbents with higher ratio of mesopores achieve higher increase in their CO<sub>2</sub> adsorption after PEI impregnation. Previous studies conducted on MCM-41 and fly ash carbons have shown that the CO<sub>2</sub> chemical adsorption for PEI impregnated materials is favored by the presence of

mesopores that can promote mass transfer within the pores. This is also consistent with the higher CO<sub>2</sub> adsorption capacity of the PEI impregnated samples at 75°C compared to that at 30°C (data not shown here).

## Conclusions

Several surface treatment methods (NH<sub>3</sub> treatment and PEI impregnation) were used in this work to modify the surface properties of carbon sorbents to improve their CO<sub>2</sub> capture capacity. NH<sub>3</sub> treatment increases both surface area and pore volume of the activated carbon made from anthracite, as well as improve the CO<sub>2</sub> capture capacity of the activated anthracites at higher temperature (50 and 75 °C). PEI impregnation dramatically reduces the surface area and pore volume of the carbon sorbents due to pore blockage and surface coverage, but it also improves the CO<sub>2</sub> capture capacity of the carbon sorbents. The carbon sorbents with higher ratio of mesopores achieve higher increase in their CO<sub>2</sub> adsorption after PEI impregnation.

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