

IMPACT OF PORE STRUCTURE AND SURFACE OXYGEN ON ELEMENTAL MERCURY UPTAKE BY VIRGIN ACTIVATED CARBON

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Introduction

Direct injection of powdered activated carbon into the flue gas stream of a coal-fired power plant has been advocated as a relatively simple approach for controlling elemental mercury emissions. Many factors influencing the efficiency of mercury removal have been reported[1]. The objective of this study was to evaluate the impact of pore structure and surface oxygen on elemental mercury uptake. Therefore, the elemental mercury uptake by three virgin and outgassed activated carbons produced from the same raw material but with different surface areas, pore structures and surface chemistries was examined in this study.

Experimental

Three activated carbon samples (A, B and C) made of the same bituminous coal but under different activation conditions were evaluated as elemental mercury sorbents. Their nitrogen adsorption isotherms were measured using the ASAP2000 (Micromeritics, Atlanta, GA) system and were used to calculate the specific surface area S_{BET} , total pore volume and pore size distribution.

Elemental mercury uptake was studied in a laboratory-scale 0.5 inch I.D stainless steel fixed-bed reactor charged with varying amounts of sorbent. A mercury permeation device manufactured by VICI Metronics (Santa Clara, CA) was used as source of elemental mercury (Hg^0) throughout the study. The mercury permeation device was sealed in a glass permeation tube holder with inlet and outlet ports. The permeation tube holder contained glass beads for heat exchange and was immersed in a temperature controlled oil bath. Elemental mercury concentration ($56 \mu g/m^3$) and carrier gas (nitrogen) flow rate (0.5 L/min) were maintained constant for all experiments in this study. Mercury uptake was measured at 140 °C to represent relevant process conditions in full-scale systems. Influent and effluent mercury concentrations were measured using the atomic absorption spectroscopy (Perkin Elmer Model 403). The outgassing was performed under argon atmosphere using Lindberg Hevi-Duty furnace with a mullite tube. The activated carbon was heated at a rate of 200 °C/h to a maximum temperature of 900 °C. This

temperature was kept for 20 hours and then cooled at a rate of 200 °C/h to room temperature. The activated carbon was used immediately after preparation to reduce oxygen chemisorption that normally occurs during storage. The breakthrough profiles and dynamic adsorption capacities for the virgin and outgassed activated carbon were studied and correlated with pore structure and surface oxygen content.

The oxygenated surface groups were determined according to the method of Boehm[2,3]. 0.05N sodium bicarbonate, 0.05N sodium carbonate, 0.05 and 0.25N sodium hydroxide, and 0.05N hydrochloric acid were prepared using RO/DI water. 70 ml of these solutions were added to 2 grams of carbon. The vials were sealed with a Teflon-lined stopper and aluminum cap and shaken for 24 hours in a rotary shaker. 15 ml of each filtrate was titrated with standardized HCl or NaOH to determine excess base or acid in the sample. The amount of surface oxides was then calculated based on the amount of base consumed by each sample.

Results and discussion

Figure 1 shows nitrogen adsorption-desorption isotherms at 77K on the three carbons used in this study. Each isotherm shows a distinct hysteresis loop, which is characteristic for porous adsorbents. The lower end of the hysteresis loop in each isotherm approximately occurs at a relative pressure of 0.4. From the point of view of the performance on a volume basis, the shapes of adsorption isotherms indicate that carbon C has significantly higher surface area and pore volume than carbons A and B. Figure 2 depicts pore size distribution of pore diameter ranging from 17 to 3000 Å. The distributions have similar shapes and the peaks are between 20-40 Å. Table 2 summarizes the surface pore characteristics of carbons A, B, and C.

Table 2 indicates that carbon C has large pore volume with mesopores and macropores being predominant, while micropores comprised only 11.5% of the total pore volume. On the other hand, carbons A and B had much larger micropore and mesopore volume than the macropore volume. This is particularly pronounced for carbon A,

where micropores constituted 62.8% of the total pore volume.

Table 1. Specific surface area and pore characteristics of activated carbons

Sample	S_{BET} (m^2/g)	V_t (m^3/g)	$V_{\text{me+ma}}$ (m^3/g)	V_{mi}/V_t (%)
A	885	0.494	0.184	62.8
B	1268	0.711	0.365	48.7
C	1446	0.936	0.828	11.5

S_{BET} : BET nitrogen surface area

V_t : Total volume;

$V_{\text{me+ma}}$: Mesopore volume + Macropore volume

V_{mi}/V_t : Micropore volume/Total pore volume

Table 2. Mercury uptake and apparent density

Sample	C_1 ($\mu\text{g mercury} / \text{g carbon}$)	C_2	C_3	$^a\text{B. D.}$ (cm^3 / g)
A	397	1076	1309	0.53
B	213	400	728	0.42
C	257	587	1180	0.32

C_1 : Particle size 12×16mesh

C_2 : Particle size 60×80mesh

C_3 : Outgassed carbon, particle size 60×80mesh

a B.D.: Bulk density

Figure 3 illustrate the breakthrough curves for the three sorbents evaluated in this study with particle size of 60×80 U.S. Mesh. Carbon A showed the highest mercury uptake capacity, while carbon B showed the lowest capacity. Figure4 illustrates the breakthrough curves of outgassed carbon with particle size of 60×80 mesh. The vapor-phase mercury uptake capacity of the carbons, as calculated by integrating the area above breakthrough curves, are listed in Table 2.

Table 2 indicates that particle size affects the adsorption capacity of carbon since the experiments with smaller particles resulted in higher adsorption capacity. Such behavior can easily be explained by the kinetic limitations of the fixed bed reactor operated at an extremely short empty-bed contact time.

Tables 1 2 also show that carbon A has lower surface area and pore volume but higher mercury uptake capacity when compared with carbon C. It is well known that besides the surface area and pore characteristics, the surface chemistry of carbon plays an important role in the adsorption of gases due to their acidic properties. The surface chemistry is governed by the amount of

heteroatoms incorporated into the carbon matrix[4]. The most important of these are oxygen, nitrogen, phosphorus, hydrogen and sulfur. They are responsible for the presence of various acidic or basic chemical functional groups. Although carbon A had the higher sulfur content than carbons B and C (0.78%, 0.53%, and 0.34%, respectively) it is unlikely that these residual sulfur that is most likely embedded deeply in the carbon structure could explain this difference in capacity.

The number of acidic sites of various species was calculated under the assumption that NaOH neutralizes carboxyl, phenolic, lactonic and carbonyl groups; Na_2CO_3 neutralizes carboxyl and lactonic groups; and NaHCO_3 neutralizes only carboxyl groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon surface. The results of these analyses are presented in Table3.

Table 3. Acidic surface functional groups obtained from Boehm titration

Sample	Surface functional groups ($\mu\text{eq/g}$)				
	Carboxylic	Lactonic	Phenolic	Carbonyl	Basic
A	0	40	49	31	552
B	0	6	33	0	535
C	0	6	0	32	535

Table 3 shows that carbon A has higher acid functional group content than B and C. The basic group content of all samples was similar. It was proposed that oxygen-containing functional group reduced adsorptive capacity by localizing free electrons of the carbon basal planes[5] and that outgassing at 900 °C removes all acidic surface functional groups[6]. Table 2 shows that the mercury uptake capacity increased for all three samples after outgassing. The increase in capacity varied from about 100% for carbon C to 19% for carbon A. These results suggest that outgassing activated carbons with greater surface area or larger pore volume will have a bigger impact on the capacity for elemental mercury. It is also possible that the negative impact of surface functional groups was counterbalanced with the large fraction of micropores in carbon A, which are energetically favorable for the adsorption of small mercury molecules.

Conclusions

The three activated carbons tested in this study were produced from the same bituminous coal using identical steam activation process. Carbon B was activated with steam one hour longer than carbon A and carbon C was activated with steam one hour longer than carbon B. These differences in activation time resulted in significant increase in surface area and pore volume (carbon C had the

largest surface area and pore volume). Most of the increase in pore volume and surface area was realized in the macropore-size range (micropore volume decreased from 62.8% to 48.7% to 11.5% with an increase in steam activation time). However, the increase in surface area and pore volume had a negative impact on mercury uptake capacity. Activated carbon with the largest fraction of micropores (carbon A) had the highest mercury uptake capacity. Although carbon A had the highest sulfur content, it is unlikely that this sulfur deeply embedded in the carbon structure could have a significant impact on mercury uptake. Removal of oxygen-containing surface functional groups by outgassing at 900 °C increased the adsorption capacity for mercury for all three sorbents. It can therefore be concluded that low acidity carbons with predominant microporosity would be most suitable sorbents for elemental mercury.

References

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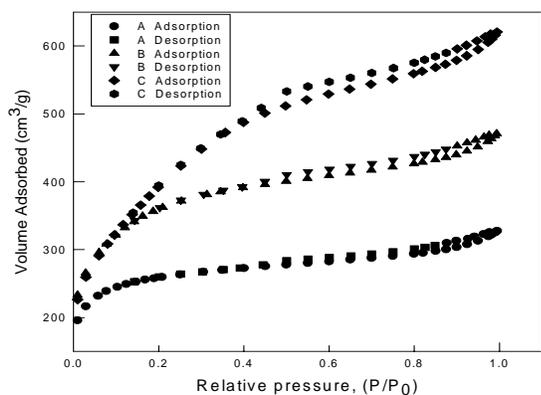


Figure 1. Nitrogen adsorption-desorption isotherms for carbons A, B, and C

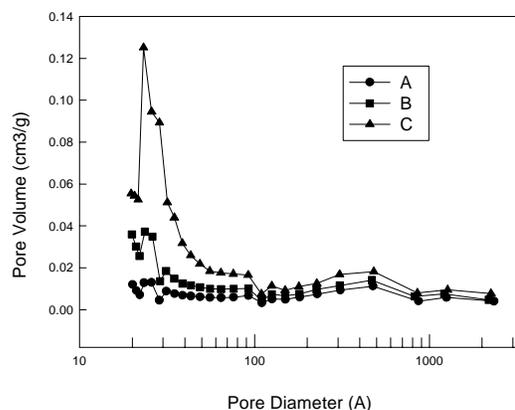


Figure 2. Pore size distribution for carbons A, B and C

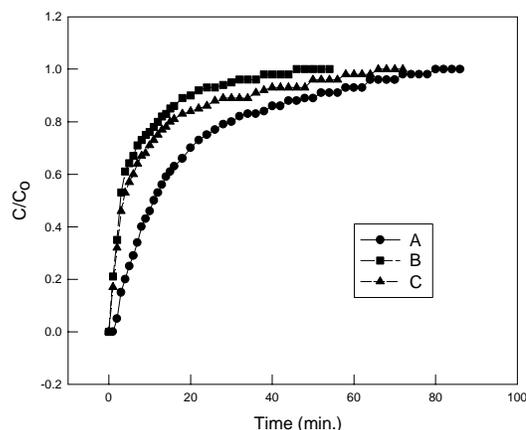


Figure 3. Mercury breakthrough for virgin carbons (0.5 g of 60x80 U.S. Mesh size)

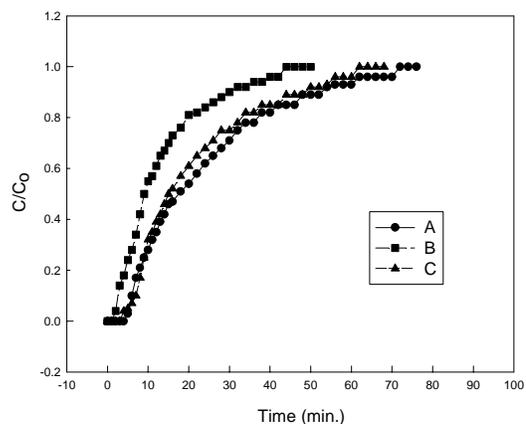


Figure 4. Mercury breakthrough for outgassed carbons (0.5 g of 60x80 U.S. Mesh size)