

SULFUR IMPREGNATION ON ACTIVATED CARBON FIBERS BY H₂S OXIDATION FOR Hg REMOVAL

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Introduction

Impregnation of sulfur can significantly improve the adsorption capacity of virgin activated carbon. This was previously tested by Vidic and co-workers [1-3]. Their studies suggested that the following factors could be important for mercury uptake onto sulfur impregnated sorbents: sulfur content, sulfur forms, sulfur distribution, and pore structure/surface area of the sorbent. Kwon et al. [1] compared the mercury adsorption capacity of BPL carbon impregnated with S through two different methods: reaction with elemental sulfur at 600°C and oxidation of H₂S at 150°C. Although less effective, Impregnation of sulfur through H₂S oxidation is generally performed at lower temperature and has significant value in the industrial ecology approach for producing effective sorbents. Sulfur impregnation of activated carbon fibers was also studied by Hsi et al. [4, 5]. Sulfur deposited on Activated Carbon Fibers (ACFs) existed in three forms, namely elemental sulfur, organic sulfur, and sulfate, with the first two forms acting as mercury adsorption sites [4]. The authors stated that both sulfur content and the micropore structure are important for the uptake of vapor phase mercury.

The objective of this study was to determine the mechanism of sulfur impregnation on carbonaceous surfaces through H₂S oxidation and to determine the sulfur forms produced. An additional objective was to understand the key parameters of sulfur impregnated sorbents for elemental mercury adsorption.

Experimental

Sulfur impregnation onto Activated Carbon Fibers (ACFs) by H₂S oxidation was conducted using a fixed bed reactor system. The gases were supplied from pressurized tanks. H₂S and O₂ (O₂: H₂S = 4:1) were diluted by N₂ to a desired concentration by controlling the flow rate of each gas with a mass flow controller. The total gas flow rate to a quartz reactor (38cm long with 1cm OD) was maintained at 150 ml/min. The reactor was positioned vertically in the middle of a tubular furnace. The effluent gases were analyzed continuously by a Quadrupole Mass Spectrometer (QMS) 300. Two sets of experiments were conducted with ACF10 and ACF25 respectively. ACF10 was

impregnated with sulfur at 80°C and 150°C until the effluent H₂S concentration reached the influent level. These samples were labeled as ACF10-80C and ACF10-150C. ACF25 was impregnated with sulfur at 150°C for 2, 6 and 24 hours. These samples were labeled as ACF25-150C-2hrs, ACF25-150C-6hrs, ACF25-150C-24hrs. The average amounts of sulfur deposited on the sorbent were determined from the breakthrough curve.

Samples before and after sulfur impregnation were characterized using the following methods: surface area and pore size distribution of virgin and impregnated ACFs were analyzed using nitrogen adsorption at 77K in a Quantachrome Autosorb Automated Gas Sorption System; SEM-EDAX analysis was conducted using a Philips XL30 SEM equipped with an EDAX detector; XPS analysis was performed using a Physical Electronics Model 550 equipped with a cylindrical, double-pass energy analyzer.

Raw and sulfur-impregnated ACFs were tested for vapor phase elemental mercury uptake at 140 °C in a fixed-bed reactor (detailed description of the experimental system can be found elsewhere [1]). Industrial grade nitrogen was used as the carrier gas with a flow rate of 600 ml/min. The inlet mercury concentration was maintained at 350 µg/m³.

Results and Discussion

The first two columns of Table 1 summarize average sulfur contents of the sorbents produced. Low temperature (e.g., 80 °C) does not facilitate significant sulfur deposition through H₂S oxidation, even if a complete H₂S breakthrough was attained. Both ACF-10 and ACF-25 achieved much higher sulfur content at 150 °C. This may be due to the fact that H₂S oxidation can only take place inside smaller pores. This hypothesis is supported by pore size distribution measurements shown in Figure 1, which depicts changes in the pore size distribution of ACF10 after sulfur impregnation at 80 °C and 150 °C. It is clear that sulfur deposition at 80 °C was accomplished by pore filling rather than by monolayer deposition as the loss of the small pores was obvious, while very few medium micropores was occupied by sulfur molecules.

Figure 2 shows changes in the pore size distribution of ACF25 as a result of sulfur impregnation at 150 °C for 2, 6 and 24 hours. It is clear that the initial losses in the pore volume after only 2 hours of impregnation occurred in small and medium pores, while large pores were not affected by sulfur deposition. The sudden loss of small micropores was also observed by Hsi et al. [4, 5]. As the impregnation time was extended to 6 hours, further reduction in small and medium pores was observed. Reduction in the large pore volume was observed only after the amount of sulfur deposited on the ACF surface exceeded 20 wt% after 24 hours of impregnation. Similar conclusion can be made for the data shown in Figure 1 and Table 1, where the sulfur content exceeded 20 wt% before filling of large micropores was accomplished.

SEM-EDAX analysis was conducted for ACFs before and after sulfur impregnation. EDAX provided the elemental compositions of the outer layer of the ACF samples, which were listed in the third column of Table 1. At 80 °C, the average sulfur content at outer surface of the ACF is much lower than that in the bulk. This means that the sulfur

tends to deposit more inside than outside of the sorbent particle at lower temperatures. The increase in temperature resulted in sulfur deposition at the outer surface, as can be seen from Table 1. ACF-25 after shorter impregnation times (2 hours and 6 hours) also exhibited lower surface coverage as compared with the average sulfur content. For longer impregnation times (24 hours), surface sulfur content was higher than the average. This behavior suggests that sulfur impregnation occurs from the inside to the outside of the adsorbent particle.

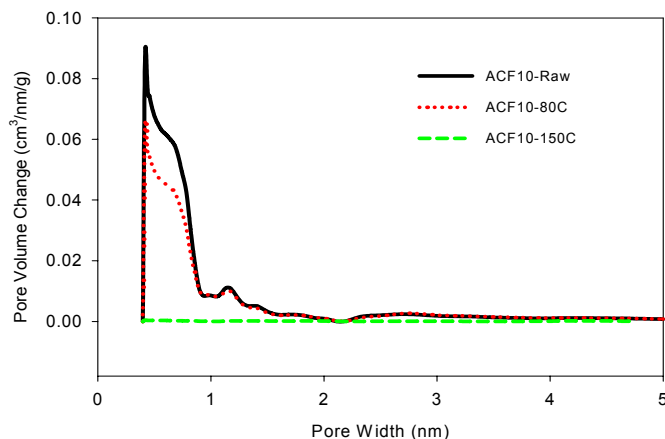


Figure 1. Pore size distribution of ACF-10 before and after sulfur impregnation at different temperatures

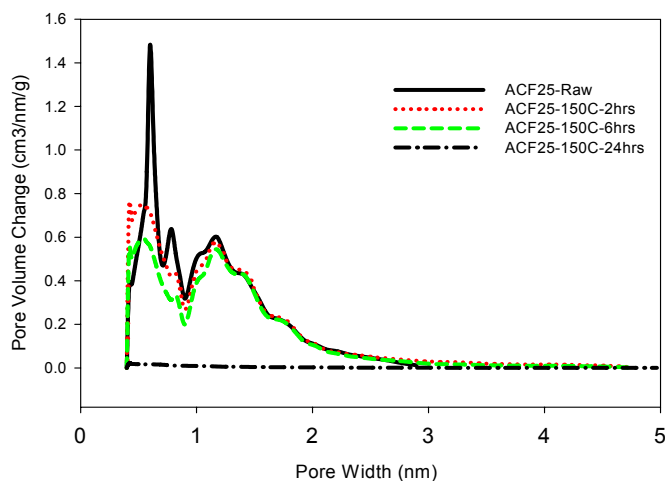


Figure 2. Pore size distribution of ACF-25 before and after S impregnation at different reaction times

Comparison of the volume of sulfur added per gram of ACFs with the loss in the pore volume can provide answers to the question of whether the loss in pore volume was due to complete filling of the pores or just blockage of the pore entrance. Table 2 summarizes the results of these calculations. None of the cases show that the lost total

pore volume occurred through complete filling of pores. The lower temperature seems to result in higher ratio of pore filling. This further supports the hypothesis that pore filling is the dominant mechanism for sulfur deposition at low temperature. At 150°C, all samples show less than 50% of the lost pore volume was actually filled. This indicates that most of the pores were blocked, rather than filled.

Table 1. Summary of Sorbent Properties and Mercury Adsorption Capacity

Sample Name	Average Sulfur Content (QMS) (wt%)	Surface Sulfur Content (EDAX) (wt%)	Total Pore Volume (>0.4 nm) (cm ³ /g)	Total Surface Area (m ² /g)	Hg Uptake Capacity (µg/g)
ACF10-Raw	0.2	0.2	0.371	920	214
ACF10-80C	6.7	1.14	0.299	710	450
ACF10-150C	26.3	34.5	0.0048	8.3	220
ACF25-Raw	0.2	0.2	0.741	1950	319*
ACF25-150C-2hrs	4.1	1.02	0.714	1880	790
ACF25-150C-6hrs	10.2	7.36	0.634	1610	480
ACF25-150C-24hrs	30.5	34.41	0.015	100	230

*standard deviation: ±8% based on three runs.

Table 2. Comparison of the Volume of Sulfur Added and the Pore Volume Loss

Samples	Average S%	S added	Volume of S added	Total pore volume Loss	% of Lost pore volume filled
	(Wt%)	(mg/g raw ACF)	(cm ³)	(cm ³)	(%)
ACF10-80C	6.7	71.8	0.037	0.05	73
ACF10-150C	26.3	356.9	0.182	0.36	50
ACF25-150C-2hrs	4.1	42.8	0.022	0.11	20
ACF25-150C-6hrs	10.2	113.6	0.058	0.15	39
ACF25-150C-24hrs	30.5	438.8	0.224	0.83	27

The sulfur forms on ACF-25 before and after sulfur impregnation were also investigated by XPS. The result shows that sulfur on ACF surface was present mainly in free elemental form with negligible amounts of oxidized sulfur forms.

Table 1 shows the sulfur content and Hg uptake capacity of each sample, which clearly indicates that higher sulfur content does not necessarily lead to higher mercury uptake. It appears that the sulfur content of around 5% deposited at 150 °C produces a sorbent with the highest mercury capacity. This is probably due to the loss of pore volume/surface area resulted from excess sulfur impregnation. Similar behavior was observed earlier [1, 6].

Conclusions

Sulfur was impregnated onto the surface of ACFs by oxidation of H₂S. Sorbents before and after sulfur impregnation were characterized and tested for vapor phase mercury adsorption. Sulfur was impregnated mainly in the form of elemental sulfur. At 150 °C, with an increase in impregnation time, sulfur fills the pores up, until there is complete

loss of the original pore volume, with an initial sudden decrease in small pore volume. At lower temperature (80 °C) and/or shorter impregnation time, pore filling seems to be the dominant mechanism for sulfur deposition. However, for all samples, the impregnation process can only be explained by a combination of pore filling and monolayer adsorption. Hg adsorption capacity first increased at low sulfur content; further increase in sulfur content actually decreased Hg adsorption capacity. This is probably due to the loss of pore volume or surface area.

References

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