

NOVEL NANOSTRUCTURED SORBENTS FOR VAPOR-PHASE MERCURY CAPTURE

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Abstract

This paper describes the development and evaluation of novel carbon, carbon composite, and non-carbon-based sorbents for vapor phase mercury capture. Elemental mercury in concentrations of $60 \mu\text{g}/\text{m}^3$ is generated in argon gas and then passed through a thermostatically controlled fixed bed reactor followed by atomic fluorescence detection of oxidized and elemental mercury. Semi-continuous breakthrough curves are measured, which provide comparative information on the adsorption capacity and kinetics for a wide range of novel nanomaterials and conventional sorbents as reference samples. These new nanostructured materials include self-assembled mesoporous carbon with varying surface treatments, sulfur nanotubes, selenium/carbon nanocomposites, and various nanophase amalgamating metals. Capacities are measured as a function of temperature from 20°C to 150°C and are compared to those for commercial activated carbons specifically optimized for mercury capture. Some of the nanomaterial formulations in this exploratory work appear quite promising for higher efficiency mercury control.

Introduction

By 2018, the EPA has mandated that mercury emissions from power plants be reduced by 70%. Mercury exposure can lead to increased risk of neurodegenerative disease in infants, impairment of speech, movement, and cognitive ability, respiratory failure, and death. Because of its toxic nature, materials that capture mercury not only in power plant flue gases but in all areas where it has accumulated are required. One of the most promising methods for the capture of mercury in power plants is adsorption on high surface area carbons that have been injected into the flue gas post-combustion. Activated carbon injection (ACI) has been shown to reduce mercury emissions by 70-90% (US EPA). Novel sorbents are being developed to increase the efficiency of the flue gas capture process, to remove mercury in soils, and to clean up spills. Sulfur effectively captures mercury in mixed solid wastes by forming HgS (Fuhrmann et. al.), and sulfur doped activated carbons vastly increase vapor phase mercury capture capabilities even while significantly reducing sorbent surface area (His et. al.). The goal of the present study is to apply the advances made in nanomaterial fabrication to the problem of mercury capture. Nanoscale sulfur and selenium are studied in comparison to mercury optimized activated carbon. Novel surface treatments of nanoscale carbons are also investigated. By investigating these materials using standardized mercury concentrations in argon gas, their relative capacities can be compared.

Experimental

Sorbents

Carbon sorbents studied include Darco FGL powdered activated carbon with a surface area of 550 m²/g, granulated activated carbon from Alfa Aesar with a surface area of 900 m²/g, a non-porous nanoscale carbon black with a surface area of 38 m²/g, and a 24 nm nominal pore diameter mesoporous carbon with a surface area of 144 m²/g synthesized using a template method (Jian et. al.). Sulfur nanotubes were created using a template method. Reagent grade sulfur powder from Sigma Aldrich was dissolved to 50% by weight in carbon disulfide. Nanochannel alumina templates with 200 nm diameter channels 60 microns thick were dipped in the sulfur solution and then dried in air. The alumina template was etched in 2M NaOH for 48 hours. The sulfur nanotubes were water-washed before drying at 60°C. The total surface area was estimated by calculation to be from 10 m²/g (outer surface only) to 20 m²/g (inner and outer surfaces). For comparison, the BET adsorption surface area of sulfur powder is 0.26 m²/g. Amorphous nanoscale selenium was generated by the reduction of sodium selenide by glutathione (Ganther). The uncontrolled growth of amorphous selenium particles was hindered by a hydrophobic support and nanoscale particles were generated (Sarin et. al.). The use of carbon black and bovine serum albumin (BSA) as hydrophobic supports or stabilizers gave rise to two nanoselenium composite sorbents. Selenium concentrations by weight were 10% for the BSA and 1% for the carbon black.

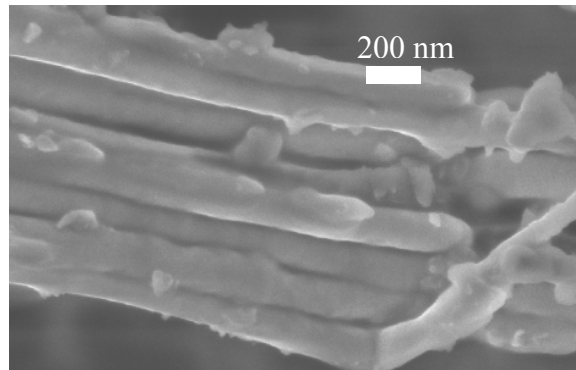


Figure 1. SEM image of sulfur nanotubes

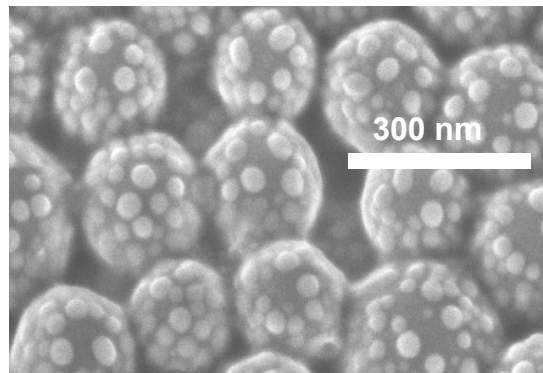


Figure 2. SEM image of nanoselenium on carbon nanospheres

Various carbon sorbents were treated with ozone as a way to functionalize their surfaces for possible increased mercury capture capacity and hydrophilicity (Gao et. al.). Carbon black, mesoporous carbon, and activated carbon were exposed to 4.5-5% or 0.16-0.22% ozone in oxygen in a fluidized bed reactor. The ozone in oxygen was generated by a CD10/AD corona discharge ozone generation system from Clearwater Tech at a flow of 216 cc/min and was diluted with 4.1 L/min of air before entering an IN-2000 LoCon UV absorption ozone analyzer from InUSA. A baseline ozone concentration was established before sorbent treatment. Reactor exit concentrations were monitored to determine the amount of ozone

that was adsorbed on the carbon. Carbon black captured 70-80% of the ozone and activated and mesoporous carbon captured virtually all of it. The ozone dose in mass ozone adsorbed per mass carbon was varied by changing the sorbent treatment time. After treatment the sorbent was flushed with oxygen for 10 min and placed under vacuum for 20 min.

Sorbent Analysis

Elemental mercury was generated in argon gas at a concentration of 60 $\mu\text{g/g}$ using the CAVKIT 10.534 from PSAAnalytical. This gas was passed through a fixed bed of sorbent suspended on a fritted glass disk in an 8 mm or 1/2 in ID tubular pyrex reactor. Bed exit mercury concentrations were determined by atomic fluorescence using the Sir Gallahad II from PSAAnalytical. The flow system consisted of 1/8 in ID PTFE tubes and PFA Swagelock fittings. Four stainless steel three way valves were used, but in general the amount of wetted stainless steel was minimized. A mass flow controller from Omega, placed directly after the analyzer, was used to maintain the gas flow at 300 cc/min. A diaphragm pump from KNF Neuberger, placed directly after the mass flow controller, was used to create a driving force for gas flow. By measuring the bed exit concentrations of elemental mercury, a semi-continuous breakthrough curve was generated giving mass mercury captured per mass sorbent. For verification, the mercury concentration in the sorbent was also determined by spectrometry after sorbent vaporization. This analysis produced capacities that differed maximally by 30%.

Results and Discussions

Mesoporous carbon and the two activated carbons were analyzed at 20-150°C. These sorbents show temperature dependence suggestive of an equilibrium or near-equilibrium adsorption process. Darco FGL has the greatest capacity because it has a high surface area and has a pore structure optimized for gas phase adsorption. Sulfur nanotubes show an increase in mercury capture capacity over powdered sulfur that is roughly proportional to their increased surface area. Unlike carbon sorbents, sulfur appears to capture mercury through a kinetically limited process that increases in rate with increasing temperature. Based on studies of the mercury capture capacities of various forms of sulfur, it is hypothesized that amorphous sulfur would show an even greater mercury capture capacity (Vidic et. al.).

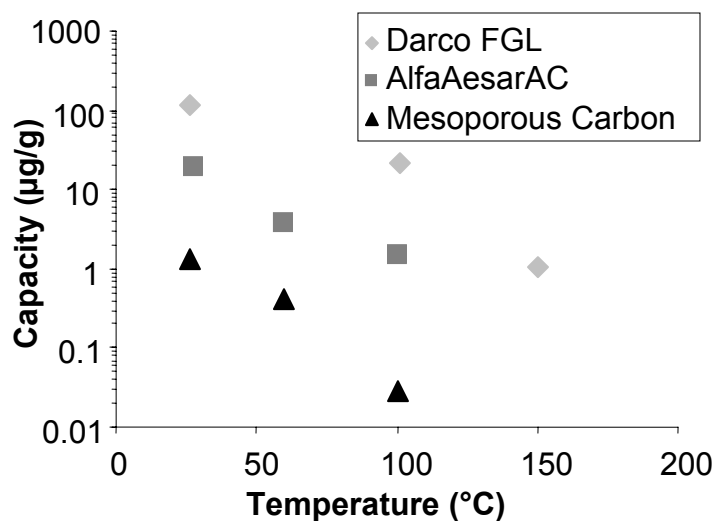


Figure 2. Mercury capture capacities of carbon sorbents

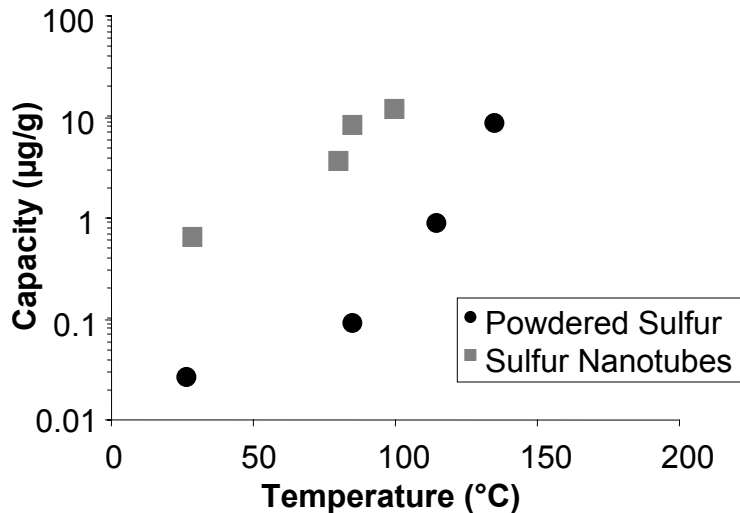


Figure 3. Mercury capture capacities of sulfur sorbents

To preserve their amorphous structure nanoselenium composite sorbents were tested at room temperature. The materials present in each sorbent were analyzed for their mercury capture capacity so that the capacity due to the selenium alone could be calculated. The full capacity of NanoSe-CB could not be determined because its ultra-high activity made it difficult to saturate the sorbent. NanoSe-CB showed a period of self activation after which it adsorbed mercury at a rate greater than any other sorbent tested.

Table 1. Room temperature capacities of selenium composite sorbents

Sorbent	Capacity, total sorbent basis (µg/g)	Capacity, selenium basis (µg/g)
NanoSe-BSA	67.2	616.2
NanoSe-CB	>352.8	>3528

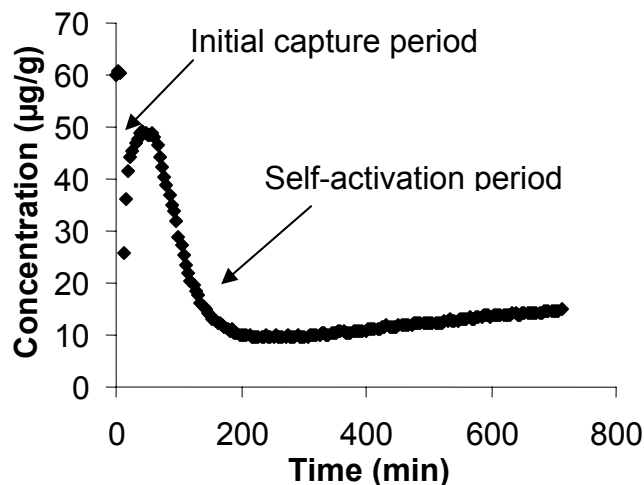


Figure 5. Breakthrough curve of NanoSe-CB showing self-activation

Mesoporous carbon was treated with ozone at two different concentrations but at similar doses. Only at high concentrations did the sorbent show an increased capacity. Under similar conditions, carbon black also showed an increased capacity. Darco FGL exhibited only a limited increase in capacity, possibly due to blockage of micropores by oxygen-containing functional groups.

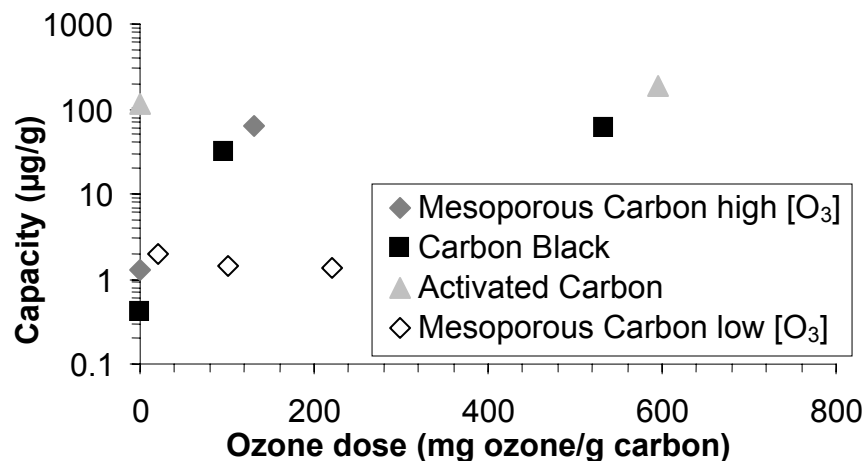


Figure 6. Room temperature mercury capacities of various ozone treated carbons at different ozone concentrations and doses

The most potentially significant finding is the large increase in Hg capacity when the high ozone concentration is used, even when the total ozone dose is similar. Ozonide has been suggested as a highly reactive surface group resulting from the treatment of carbon by concentrated ozone (Wong et. al.). This treatment has been used as an intermediate to further functionalize carbon surfaces. Further work is required to test the hypothesis that the increased capacity is the result of an oxidizing surface group like ozonide or peroxide, and then to exploit this high activity in an engineered carbon sorbent.

Aging studies of high concentration ozone treated carbon black were carried out in a number of environments as a means of understanding the stability of the ozone treatment with time. The treated sorbent was left in air, flushed with nitrogen, and flushed with nitrogen that had been bubbled through water. A large capacity decrease over 24 hours was observed for the sorbent left in air, and a similar decrease was observed for the sorbent that was flushed with nitrogen and water vapor. The sorbent that had been flushed with pure nitrogen retained much of its capacity after 24 hours. These results point to air and more specifically water vapor as the component that reacts with the treated carbon surface to decompose the capacity enhancing surface functional group. These results are consistent with an ozonide surface functional group, as ozonides are easily cleaved by water to form ketones.

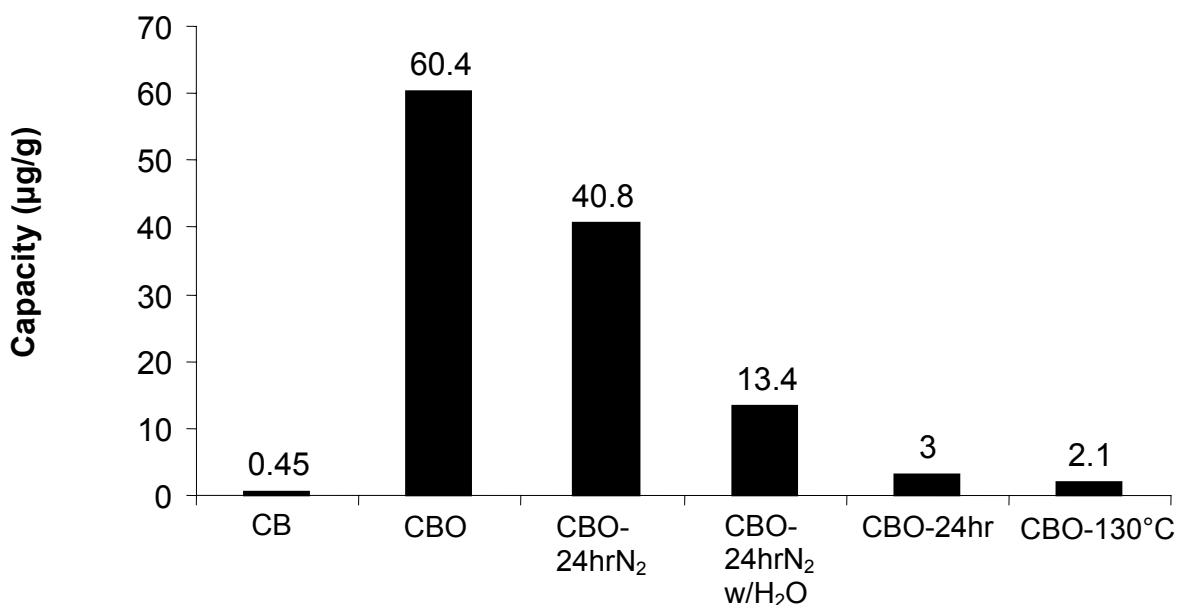


Figure 7. Mercury capture capacities of ozone treated carbon blacks after various aging treatments. CB is the capacity of the untreated carbon black. CBO is the capacity of the ozonated carbon black immediately after initial treatment. CBO-24hr is the capacity after 24 hours in air. CBO-24hrN₂ is the capacity after 24 hours flushed with nitrogen. CBO-24hrN₂w/H₂O is the capacity after 24 hours flushed with nitrogen bubbled through water. CBO-130°C is the capacity at 130°C after being stabilized in air at that temperature for 15 minutes.

Regardless of the surface functional group, ozone treatment is shown to increase carbon's ability to capture mercury. Even at 130°C the capacity of ozone treated carbon black still exceeds the untreated room temperature capacity by roughly a factor of five. A typical carbon near equilibrium physical adsorption mechanism would lead to a decrease in capacity with temperature. The ozone treatment must significantly alter the way in which carbon captures mercury, giving it an increased capacity at temperature.

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