

Supporting Information

Roles of Sulfuric Acid in Elemental Mercury Removal by Activated Carbon and Sulfur-impregnated Activated Carbon

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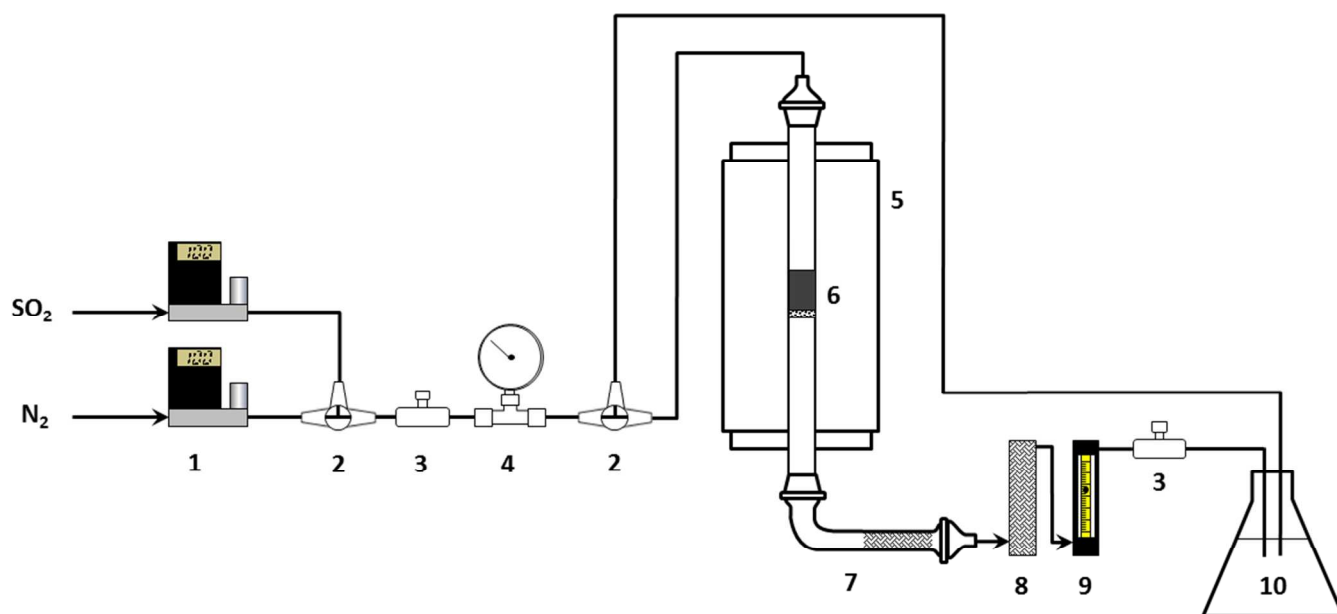


Figure S-1. Apparatus used for high-temperature reaction of Calgon BPL with SO₂. LEGEND: 1. Mass flow controllers; 2. 3-way stopcock; 3. Gas sampling port; 4. Pressure gauge; 5. Tube furnace; 6. Coke sample; 7. Sulfur collector; 8. Secondary particulate filter; 9. Flowmeter; 10. NaOH scrubbing solution.

SO₂ treatment procedure

The apparatus used for SO₂ treatment of Calgon BPL is shown in Figure S-1. SO₂ (99.95%) and N₂ (99.997%) were supplied by cylinders and each set to flow at 100 cm³ min⁻¹ by Aalborg mass flow controllers. Teflon 3-way stopcocks were used both to combine the two gases and to divert flow around the reactor when needed. The reactor was a quartz tube 68 cm in length and 2 cm inner diameter with a porous quartz disc located at the midpoint. Approximately 10 g of BPL was placed on this disc, resulting in a cylindrical bed 3.1 cm in height and 9.7 cm³ in volume. The reactor tube was positioned within a Carbolite vertical tube furnace and connected to the gas lines via ball-and-socket joints sealed with high-temperature vacuum grease. The lower connector was an L-shaped Pyrex tube stuffed with aluminum oxide wool, which functioned as a condenser and filter for elemental S produced during reaction. To ensure integrity of flow, a pressure gauge placed upstream of the reactor and a flowmeter

located downstream were monitored throughout the experiment. All gases flowed through a concentrated sodium hydroxide (NaOH) scrubbing solution prior to venting.

The reactor was first flushed with pure N₂ for 15 minutes. The furnace was then set to 120°C to drive out moisture for an additional 15 minutes. Gas flow was then diverted around the reactor as SO₂ was introduced. Gas samples were taken from the inlet sampling port and analyzed using gas chromatography until SO₂ was stable at 50 vol% to within ± 3 vol%, after which the temperature was increased to 700°C. When this temperature was reached, the 3-way stopcock was turned to introduce the 50 vol% SO₂ gas mixture into the reactor, starting the reaction. At the end of the experiment (20 minutes), SO₂ was immediately shut off and the reactor allowed to cool under flowing N₂. The treated BPL sample was then weighed to determine sample yield.

Vapor phase experiments

For each of the two sample series, approximately 0.1 g of each sample was weighed into 3 ceramic crucibles, one for the raw and 2 for the H₂SO₄-impregnated samples. All 3 crucibles were placed within a 0.7 L glass desiccator flask along with another crucible containing a small drop of liquid Hg. The desiccator was placed within a Barnant muffle furnace set to a temperature of 100, 150, or 200°C. These temperatures were chosen to emulate thermal conditions typically observed downstream of coal-fired utility boilers. As the furnace was heating, the top of the desiccator was left slightly ajar to relieve pressure build-up. When the desired temperature was reached, the lid was sealed using Zetex gloves and high-temperature vacuum grease which had been applied beforehand. All experiments were performed in air with the Hg vapor concentration assumed to be at or near to saturation.

Samples were taken at various intervals during the adsorption experiment. The desiccator was taken out of the furnace and the lid removed promptly within a fume-hood. Small amounts of roughly 20 mg were removed from each crucible with a microspatula and placed in borosilicate vials. For the BPL series, this was done after 7, 17, 24, 48, and 72 hours of mercury contact. For the SO₂-BPL series,

samples were extracted after 6, 24, 48, and 72 hours.

Vapor phase adsorption experiments to be done in the absence of O_2 were done by suspending two crucibles (one containing a carbon sample, the other containing a small drop of liquid Hg) within a vertical tube furnace. Pure N_2 was flushed through the chamber at $200\text{ cm}^3/\text{min}$ for 1 hour to purge O_2 , then the furnace temperature was raised to 200°C . When this temperature was reached, stopcocks were used to seal off the system at the top and bottom. The sample was removed after 3 days, and no intermediate lengths of time were studied.

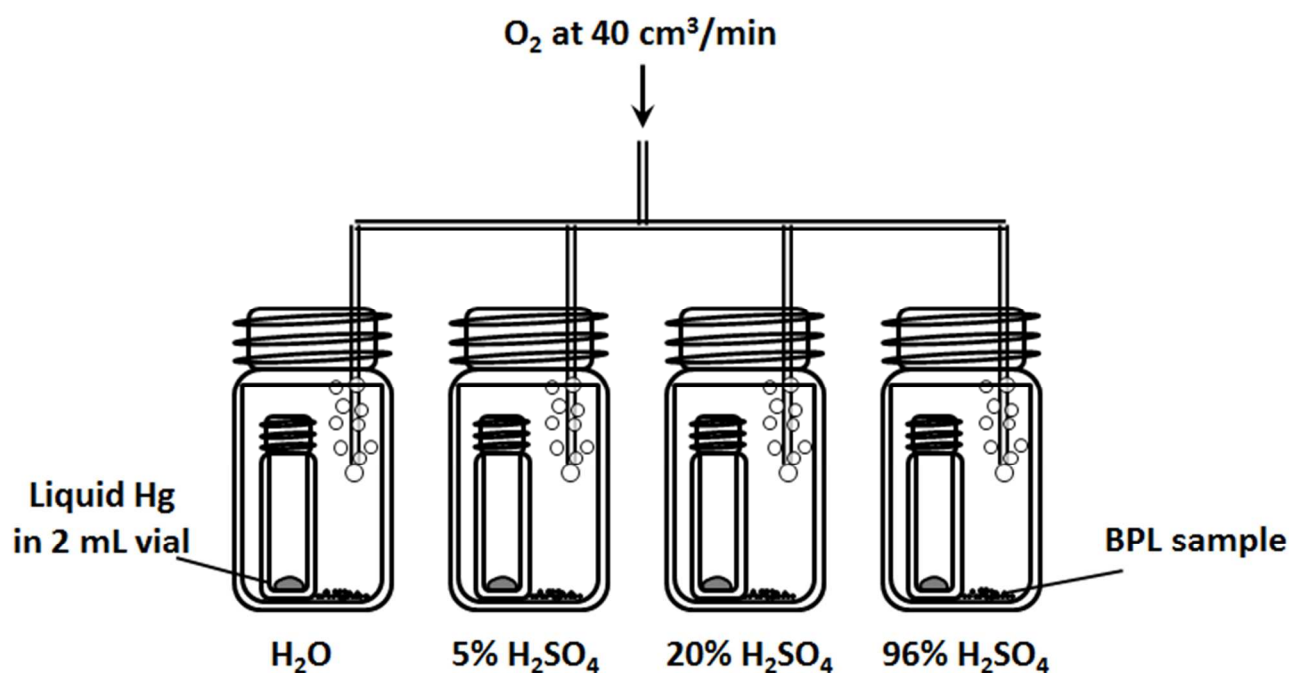


Figure S-2. Apparatus used for liquid-phase Hg uptake experiments involving addition of activated carbon and oxygen.

Liquid phase experiments

Four 20 mL borosilicate vials were tared and a small drop of Hg weighing approximately 0.1 g was placed in each. Each vial was filled to capacity with a different H_2SO_4 solution: deionized water, 5.4 wt% H_2SO_4 , 20.1 wt% H_2SO_4 , and reagent grade (~ 96 wt%) H_2SO_4 . If the experiment required the

system to be oxygen-deficient, pure N₂ was blown across the surface of each vial for 30 seconds before it was tightly capped. Experiments in which O₂ was required either had the caps left off completely or had pure O₂ bubbled into each solution at approximately 10 cm³/min. O₂ was provided by a cylinder and the flowrate set to 40 cm³/min using an Aalborg mass flow controller. The inlet was split into 4 lines consisting of 1.6 mm ID Teflon tubing. The depth of each branch of tubing within the liquid was carefully adjusted so that a nearly equivalent rate of bubble formation was seen in each vial. For all experiments, samples were held in their respective conditions for 3 days, after which the H₂SO₄ solution was separated from the Hg by decanting.

For experiments investigating the effect of a carbon surface, approximately 0.1 g of BPL was first placed in the 20 mL vial, followed by the solution. To facilitate its removal, liquid Hg was placed within an open 2 mL vial completely submerged within the solution. For all work using carbons, O₂ was bubbled into the solution. A diagram of the experimental apparatus is available as supporting information.

Sample analysis

Carbon samples from the vapor phase experiments were weighed to approximately 10 mg in 50 mL polypropylene centrifuge tubes. For the liquid phase experiments involving carbon, the entire contents of the 20 mL vials were first transferred into centrifuge tubes and then centrifuged at 1500 rpm for 10 minutes. The liquid portion was decanted and set aside for later use. 10 mL of aqua regia was then added to all samples, which were left to digest overnight. The next day, samples were placed in a water bath shaker at 45°C and 150 rpm for 3 hours. Each sample was then filled to 25 mL with deionized water and centrifuged at 1500 rpm for 5 minutes, after which the liquid portion was decanted into a 250 mL volumetric flask. The remaining sample was rinsed with 25 mL deionized water twice, each time centrifuging and decanting into the 250 mL flask. The liquid portions of the liquid phase samples set aside previously were then added to the appropriate flasks. After adding 5 mL of HCl to

every sample, the solutions were diluted to 250 mL with deionized water. Aqueous phase samples not involving carbon were simply diluted to 250 mL after adding 5 mL HCl. All samples were stored in glass test tubes until they were analyzed, at which point they were transferred to 15 mL polypropylene centrifuge tubes.

Total Hg in the samples was measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 7300. This device was calibrated using standards produced through dilution of a 1000 mg/L certified stock solution. Pore size distributions were determined using nitrogen adsorption at 77 K with a Quantachrome Autosorb-1-C. Forty adsorption points were determined between relative pressures of 0.025 and 0.995 and analyzed using a combination of quenched solid density functional theory (QSDFT) and the BJH technique. QSDFT was used for pores less than 35 nm in diameter since it is the preferred technique for micropores. Above this size QSDFT is invalid, so BJH was necessary.