Removal of Mercury from Aqueous Streams of Fossil Fuel Power Plants Using Novel Functionalized Nanoporous Sorbents

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Abstract

A new class of hybrid nanoporous materials has been developed at the Pacific Northwest National Laboratory for removing toxic heavy metals such as mercury from aqueous and nonaqueous waste streams. These novel materials consist of functional molecules capable of selectively binding mercury (thiol groups) covalently bound (as densely populated monolayers) to the synthetic nanoporous substrates. Tests indicated that this sorbent (Self-Assembled Monolayers on Meso-porous Silica—SAMMS) can achieve mercury loading as high as ~635 mg/g. The high affinity for Hg adsorption by this material was reflected by Kd values as high as 3.5 × 10⁸ ml/g. Data indicated that SAMMS can adsorb both inorganic and organic forms of mercury. Experimental data indicated that mercury adsorption performance of SAMMS was not significantly affected by pH, ionic strength, presence of other cations (Na, Ca, Cd, Cu, Fe, Ni, Pb, and Zn), and complexing anions (Cl, CN, CO₃, SO₄, and PO₄) in solution. Adsorption kinetics studies indicated that SAMMS adsorbed mercury very rapidly (about 99.9% adsorption occurring within first five minutes). Tests conducted using samples of different aqueous and nonaqueous waste streams have confirmed the exemplary performance characteristics of SAMMS sorbents. Preliminary cost estimates indicated that using SAMMS would result in significant savings in mercury remediation costs as compared to the use of conventional adsorbents such as ion exchange resin and activated carbon.

Introduction

There is a significant need for a technology to remove toxic constituents such as mercury, arsenic, and selenium from aqueous effluents of coal-fired power plants such as, blow down water, wet scrubber effluents, and ash pond waters. These effluents typically contain high concentration of dissolved major and dissolved toxic constituents, and exhibit a wide range of pH values (~4 – 12 SU). There are a number of existing technologies for mercury removal from water and wastewater. These include, sulfide precipitation, coagulation/coprecipitation, adsorption, ion exchange, and membrane separation. Recent reviews have included detailed discussion of the performance characteristics, advantages and disadvantages of these treatment methods⁴⁻⁵. These reviews indicated that there is a need for a new mercury removal technology that overcomes the significant process, performance and cost-related shortcomings of these conventional technologies.

To meet this need we have designed and developed a new class of high-performance nanoporous sorbent materials for heavy metal removal that overcomes the deficiencies of existing technologies. These novel materials are created from a combination of synthetic mesoporous ceramic substrates that have specifically tailored pore sizes (2 to 10 nm) and very high surface areas (~1000 m²/g) with self-assembled monolayers of well-ordered functional groups that have high affinity and specificity for specific types of free or complex cations or anions (Figure 1).

Typically, the nanoporous supporting materials are synthesized through a co-assembly process using oxide precursors and surfactant molecules. The synthesis is accomplished by mixing surfactants and oxide precursors in a solvent and exposing the solution to mild hydrothermal conditions. The surfactant molecules form ordered liquid crystalline structures, such as hexagonally ordered rod-like micelles, and the oxide materials precipitate on the micellar surfaces to replicate the organic templates formed by the rod-like micelles. Subsequent calcination to 500 °C removes the surfactant templates and leaves a high surface area nanoporous ceramic substrate. Using surfactants of different chain length produces nanoporous materials with different pore sizes.

These nanoporous materials can be used as substrates for self-assembled monolayers of adsorptive functional groups that are selected to specifically adsorb heavy metals. Molecular self-assembly is a unique phenomenon in which functional molecules aggregate on an active surface, resulting in an organized assembly having both order and orientation. In this approach, bifunctional molecules containing a hydrophilic head
Materials and Methods

A series of experiments were conducted to establish the mercury adsorption performance as function of pH, ionic strength, competing cations, and complexing ligands. Comparative tests were conducted to measure the kinetics of mercury adsorption. Detailed descriptions of the synthesis, fabrication, and adsorptive properties of these novel materials have been published previously.

Adsorption experiments were conducted by contacting known quantities of thiol-SAMMS material with 0.1M sodium nitrate solutions containing mercury (II) added as a nitrate salt. The initial concentrations mercury ranged from 17–800 mg/L, and the solution to sorbent ratio was fixed at 5000 mL/g. A similar set of experiments was conducted to examine the adsorption of the most toxic form of mercury, namely, the methylated form (CH$_3$Hg$^+$). In this experiment, 10 mg quantities of thiol-SAMMS was contacted with 50 mL aliquots of 0.1M sodium nitrate solution containing methyl mercury (CH$_3$HgOH) in concentrations ranging from $\sim$12 – 360 mg/L. The suspensions in both sets of experiments were continuously shaken and allowed to react under ambient temperature conditions ($\sim$25°C) for approximately 8 hours. Next, the sorbent and the contact solutions were separated by filtration and the residual mercury concentrations in aliquots of contacting solutions were measured by using inductively-coupled plasma mass spectrometry (ICP-MS). The adsorption parameters were derived by fitting the data with the linearized form of Langmuir isotherm,

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b}$$

Where, C is the residual metal concentration in mg/L, x/m is the adsorption density in mg/g, b is the adsorption maximum (mg/g), and K is the Langmuir Affinity constant (g/L).

The selectivity of a sorbent for a contaminant is typically expressed as a distribution coefficient (K$_d$ ml/g) which defines the partitioning of the contaminant between sorbent and solution phase at equilibrium. Distribution coefficient is the measure of an exchange substrate's selectivity or specificity for adsorbing a specific contaminant or a group of contaminants from matrix solutions, such as waste streams. The distribution coefficient (sometimes referred to as the partition coefficient at equilibrium) is defined as a ratio of the adsorption density to the final contaminant concentration in solution at equilibrium. This measure of selectivity is defined as

$$K_d = \frac{m}{v}$$

Where, K$_d$ is the distribution coefficient (ml/g), (x/m)$_{eq}$ is the equilibrium adsorption density (mg of contaminant per gram of adsorbing substrate), and c$_{eq}$ is the contaminant concentration (mg/ml) in contacting solution at equilibrium.

Adsorption kinetic experiments were conducted by contacting 200 mg of thiol-SAMMS with a 0.1 M NaNO$_3$ solution spiked with 10 mg/L concentration of mercury. The mixture was stirred constantly, and periodically aliquots of solution were drawn to monitor the residual mercury concentration. For comparison, mercury adsorption kinetic performance of a resin (GT-73) was also studied.

The effect of pH on mercury adsorption was tested by adjusting the pH (2–10) of a series of aliquots of 0.1M NaNO$_3$ solution each spiked with 0.09 mM of mercury. The effect of ionic strength on mercury adsorption was assessed by using a series of mercury-containing (~0.09mM) NaNO$_3$ solutions with ionic strength ranging from 0.1–4 M. For control, deionized distilled water containing only mercury was used with the resulting ionic strength of 0.0003M.

The experiment to assess the effect of competing cations on mercury adsorption consisted of 100 mM sodium nitrate solution containing ~0.09 mM of mercury and equimolar (~0.09 mM each) concentrations of four [Ca, Cu(II), Fe(II), Pb] and seven [Ca, Cd, Cu(II), Fe(II), Ni, Pb, Zn] cation mixtures equilibrated with thiol-SAMMS sorbent. The adsorption of