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MERCURY SEPARATION AND IMMOBILIZATION USING SELF-ASSEMBLED MONOLAYERS ON MESOPOROUS SUPPORTS (SAMMS)

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ABSTRACT

Mercury (Hg) is one of the most toxic metals found in the environment. The purpose of this study was to investigate the performance of an innovative technology, self-assembled monolayers on mesoporous supports (SAMMS), in separating and immobilizing Hg from aqueous solutions. The high surface area of the mesoporous silica and the covalent binding between the thiol (-SH) group in SAMMS and Hg in solution provide SAMMS with distinctive advantages over existing technologies. The results show that (i) the Hg removal is kinetically quite rapid, (ii) the sorption data follow Langmuir isotherms, (iii) the maximum sorption capacity could be up to 613 mg of Hg per gram of SAMMS, (iv) SAMMS was able to reduce Hg concentrations to below the national pollution discharge emission standard level (12 ppt), (v) the Hg-laden SAMMS was stable in aqueous solution at 70°C, and (vi) the Hg-laden SAMMS was able to pass TCLP (Toxicity Characterization Leaching Procedure) tests of the U.S. Environmental Protection Agency. The results, therefore, suggest that SAMMS has a strong potential to be used for the removal and immobilization of Hg and that the Hg-laden SAMMS is suitable for long-term disposal.

INTRODUCTION

Mercury (Hg) has a crustal abundance of 0.08 ppm (80 ppb), mainly associated with sulfur. The primary source of Hg is the sulfide ore, cinnabar, and red HgO. Mercury

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is commonly extracted as the by-product of processing complex ores that contain mixed sulfides, oxides, and chloride minerals. Another source is waste recovery, which has become increasingly important.

Although the use of Hg is declining because of concern over its toxicity to humans and the ecosystem, this metal has been used in the electrochemical industry as the mobile cathode in the chloralkali cell in the production of caustic from brine. It is also widely used in electrical and measuring apparatus (e.g., thermometers, barometers, flowmeters, batteries, lamps, and electrical switches). Mercury compounds have been used in paints, pharmaceuticals, cosmetics, as seed dressings and catalysts. Dental fillings also consist of significant amounts of elemental Hg. The uses of Hg and its compounds have generated a large quantity of Hg-containing wastes/wastewater and caused contamination of soil and water resources. For example, the removal/stabilization of Hg has become one of the top environmental cleanup priorities of the U.S. Department of Energy (1, 2).

Existing technologies for Hg removal from diluted wastewater include sulfur-impregnated carbon (3), microemulsion liquid membranes (4), ion exchange (5), and colloid precipitate flotation (6). Each of these technologies has its own advantages in certain applications. For the applications discussed in this paper, an innovative technology, self-assembled monolayers on mesoporous supports (SAMMS), may have unique properties (7). In the sulfur-impregnated carbon process, Hg loading is as high as that with SAMMS. However, the adsorbed Hg may need secondary stabilization because the metal-laden carbon does not have the desired long-term chemical stability. In addition, many of the pores in the activated carbon are large enough for the entry of microbes to solubilize the Hg-sulfur compounds in the longer term although Hg-loaded carbon may pass the Toxicity Characteristic Leaching Procedure (TCLP) of the U.S. Environmental Protection Agency (USEPA) (8) immediately after Hg adsorption. The microemulsion liquid-membrane technique uses an oleic acid microemulsion liquid membrane containing sulfuric acid as the internal phase to reduce the wastewater Hg concentration from 460 ppm to 0.84 ppm (4). However, it involves multiple steps of extraction, stripping, demulsification, and recovery of mercury by electrolysis with use of large quantities of organic solvents. The liquid-membrane swelling has a negative impact on extraction efficiency. The slow kinetics of the metal-ion exchanger reaction require long contacting times. This process also generates large volumes of organic secondary wastes. The ion-

exchange process (5) uses Duolite™ GT-73 ion-exchange organic resin to reduce the Hg level in wastewater from 2 ppm to less than 10 ppb, but the oxidation of the resin can substantially reduce both the life span of the resin and its ability to remove Hg to below regulatory requirements. The Hg loading is also limited. In addition, the Hg-laden organic resin may not have the capability for resisting microbe attack. Mercury can be released into the environment if it is disposed of as a permanent waste form. The reported removal of USEPA's Resource Conservation and Recovery Act (RCRA) metals from water by colloid precipitate flotation reduced Hg concentration from 160 ppb to about 1.6 ppb (8). This process involves the addition of HCl to adjust the wastewater to pH 1, addition of Na_2S and oleic acid solutions to the wastewater, and removal of colloids from the wastewater. The treated wastewater can potentially be contaminated with Na_2S, oleic acid, and HCl from the treatment process. The separated Hg needs further treatment to be stabilized as a permanent waste form.

Because of the shortcomings of the current Hg removal technologies, the objective of this paper is to test the performance of innovative SAMMS technology in the separation and immobilization of Hg from aqueous solutions.

EXPERIMENTAL

Materials

The SAMMS technology has been described in detail by Feng et al. (7) and will only be summarized below. The technology is based on the combination of self-assembled functional monolayers (the thiol, -SH, group) and mesoporous oxides. The self-assembled functional group provides three important functions: (i) molecular recognition for metals; (ii) covalent bonding to the support materials; and (iii) high population density of the functional groups on the substrate surfaces. The mesoporous oxides provide large substrate surfaces for the functional groups.

Molecular self-assembly is a unique phenomenon in which functional molecules aggregate on an active surface, resulting in an organized assembly of molecules with both order and orientation (9–11). In this approach, bifunctional molecules containing a hydrophilic head group and a hydrophobic tail group adsorb onto a substrate or an

interface as closely packed monolayers. The driving forces for the self-assembly are the intermolecular and intramolecular interactions between the functional molecules. Both the tail group and the head group can be chemically modified to contain certain functional groups to promote covalent bonding between the functional organic molecules and the substrate on one end, and molecular bonding between the organic molecules and metals on the other. By populating the outer interface with functional groups, an effective means for scavenging heavy metals is made available. The metal-loading capability is determined by the available surface area of the underlying inorganic support. A high-surface-area support allows for high metal loadings.

The unique mesoporous oxide supports provide high surface areas of up to 1000 m^2/g (12–16), thereby enhancing the SAMMS metal-loading capacity. They also provide an extremely narrow pore-size distribution, which can be specifically tailored from 15 to 200 Å, thereby minimizing biodegradation from microbes and bacteria.

The mesoporous supporting material used in this research is SiO_2-based and is synthesized through a coassembly process using oxide precursors and surfactant molecules. The materials synthesis is accomplished by mixing surfactants and oxide precursors in a solvent and reacting the solution under mild hydrothermal conditions. The surfactant molecules form ordered liquid-crystalline structures, such as hexagonal 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 oxide skeleton. The pore size of the mesoporous materials is then determined by the rod-like micelles, which are extremely uniform. Using a different-chain-length surfactant produces mesoporous materials with different pore sizes.

The final SAMMS product is a white powder, having more than 80% surface coverage with functional groups. Its particle size is about 5 to 10 μm. The pore size within the SAMMS particles is about 5 nm. The surface area measures 871 m^2/g. Both the surface area and the pore size were measured using an Autosorb Degasser (Quantachrome).

In the kinetic experiments described below, the commercially available organic resin, Duolite™ GT-73, was used for comparison.

Sorption Kinetics

The experiments involved two starting Hg concentrations of ~0.5 and ~10 ppm in 0.1 *M* $NaNO_3$. A total of 0.24 g of SAMMS or Duolite™ GT-73 was weighed into 500-mL bottles. A 500-mL sample of the Hg solutions was added to each bottle. The solution-to-SAMMS ratio was approximately 2080 mL/g in each test. The bottles containing these slurries were shaken on an orbital shaker at 150 oscillations/min at room temperature (20 ± 2°C) for 8 h. From each bottle, a 10-mL aliquot of the well-mixed slurry was sampled at intervals of 5, 10, 30, 60, 180, 360, and 480 min, and the aliquots were filtered immediately using a 10-mL plastic syringe mounted on a filter holder containing a 0.2-μm membrane filter. The filtrates were acidified with 0.08 mL of concentrated HCl and were analyzed for total Hg concentration. Mercury was analyzed using a CETAC M-6000A Hg analyzer system with a detection limit of 10 ppt. A set of Hg solutions without the addition of SAMMS was also treated in the same way as the SAMMS slurries to serve as controls.

Sorption Isotherm

The SAMMS was prewetted in deionized H_2O to make a slurry of approximately 5 mg solid per milliliter. By pipetting, 10-mg samples of SAMMS were added to 50-mL polypropylene centrifuge tubes containing variable amounts of 0.1 *M* $NaNO_3$ solution. An aliquot containing various quantities of 0.1 *M* $Hg(NO_3)_2$ was added to each centrifuge tube containing the SAMMS to obtain initial Hg concentrations of 0 to approximately 1.5×10^{-3} *M* (300 ppm). The final volume of the solutions in each test was 50 mL. The slurries were then shaken on an orbital shaker at 150 oscillations/min at room temperature (20 ± 2°C) for 4 h to reach equilibrium before they were filtered, acidified, and analyzed for Hg as described above. The test at each Hg concentration was conducted in triplicate, and the sorption isotherm experiment was also performed using $HgCl_2$ as the Hg source.

Stability of Hg-Laden SAMMS

The leaching and hydrothermal stabilities of Hg-laden SAMMS were experimentally evaluated. The leaching solution used in the experiments was an acetic acid solution of pH 5, which is one of the solutions used in USEPA's TCLP tests.

Hydrothermal stability testing was conducted by measuring the Hg concentrations in solution after Hg-laden SAMMS was heated in deionized water at 70°C for 24 h. A Hg-laden sample was first washed with deionized water before drying in air. Subsamples of 0.05 g dried SAMMS were added to 50.0 mL deionized water in Teflon vessels, mixed well, and kept in a water bath at 70°C for 24 h. At the end of this period the solutions were filtered and the filtrate was acidified and analyzed for Hg. The tests were run in duplicate. Duplicate runs at room temperature (RT), in which the experimental conditions were the same as in the hydrothermal experiments except for the temperature, were also carried out to detect any desorption of surface-adsorbed Hg.

RESULTS AND DISCUSSION

Sorption Kinetics and Selectivity

For the 500-ppb Hg solution, Figure 1A shows that SAMMS, at a solution-to-SAMMS ratio of 2080, reduced the solution Hg concentration to less than 0.5 ppb within 5 min, and to 10 ppt within 6 h. The 10-ppm Hg concentration decreased to 3.1 ppb within 5 min to 1.6 ppb in 10 min, and then stabilized at about 1.2 ppb (Figure 1B). The corresponding kinetic behavior of Duolite™ GT-73, a commercial resin, is also shown in Figure 1, which indicates that the removal of Hg from aqueous solution by SAMMS is dramatically faster than that by the Duolite™ GT-73.

The selectivity of SAMMS for Hg can be illustrated by the Hg distribution coefficient (K_d). The distribution coefficient was calculated as follows:

$$K_d = A/C, \quad (1)$$

where A is the amount of Hg adsorbed by SAMMS or the GT-73 resin (μg/g) and C is the equilibrium Hg concentration (μg/mL). Table 1 shows that the K_d values were variable, depending on the Hg concentrations, ranging up to 10^8 mL/g for SAMMS in aqueous solutions containing 0.1 *M* $NaNO_3$. It also suggested that the selectivity of SAMMS for Hg was approximately a factor of 1000 higher than that of the GT-73 resin.

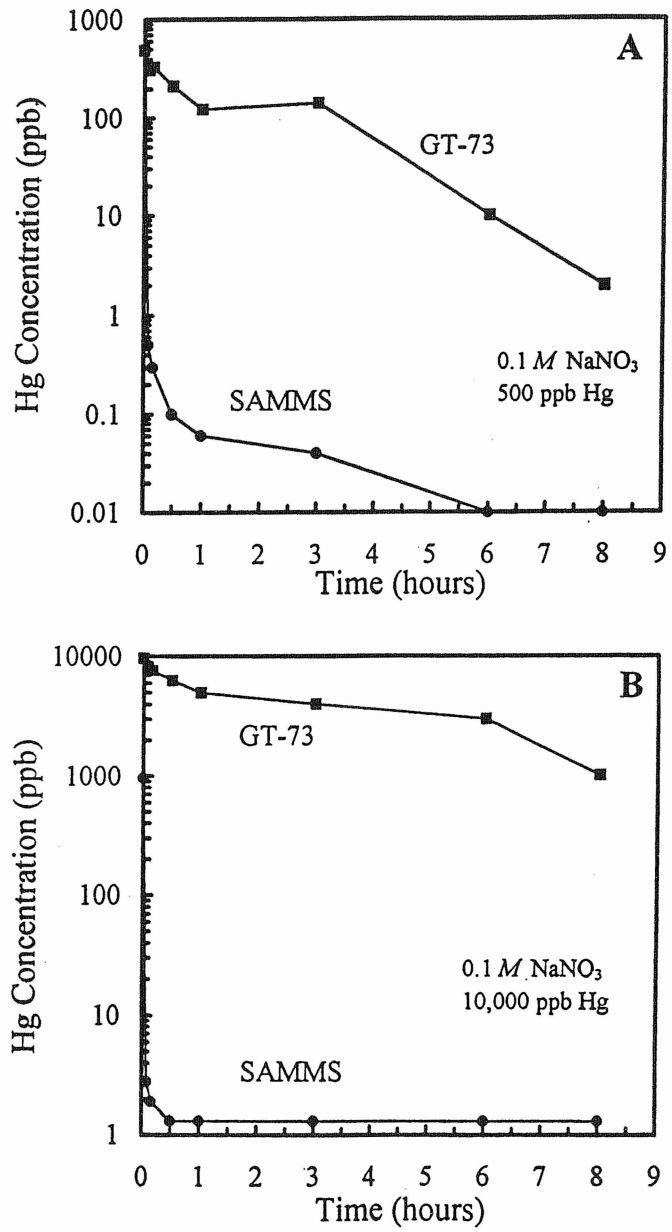

FIGURE 1. Changes of Hg concentrations as a function of time in the sorption reactions of SAMMS and Duolite™ GT-73 with initial Hg solutions of 500 ppb (A) and 10,000 ppb (B).

TABLE 1. MERCURY DISTRIBUTION COEFFICIENTS (K_d) IN SAMMS AND DUOLITE™ GT-73 AS A FUNCTION OF CONCENTRATION

Initial Hg (ppm)	Final Hg (ppm) (SAMMS)	Final Hg (ppm) (GT-73)	K_d (mL/g) (SAMMS)	K_d (mL/g) (GT-73)
0.487	1.0×10^{-5}	2.0×10^{-3}	1.01×10^{8}	5.05×10^{5}
9.70	1.2×10^{-3}	1.01	1.68×10^{7}	1.79×10^{4}

Sorption Isotherm

The equilibrium Hg-loading capacity of SAMMS is dependent on mercury concentrations and complexing ligands in the liquid phase. Figure 2 illustrates the sorption behavior for using both $Hg(NO_3)_2$ and $HgCl_2$ as the Hg source in 0.1 *M* $NaNO_3$ matrix solutions containing different amounts of mercury. In each case, the experimental results exhibited a Langmuir isotherm curve (see Figure 2A).

The Langmuir isotherm has the following general form:

$$C_F/C_S = 1/Kb + C_F/b, \quad (2)$$

where C_F is the equilibrium concentration of Hg (mg/L), C_S is the amount of Hg sorbed on the SAMMS surface (mg/g), K is the Langmuir adsorption constant (L/mg), and b is the maximum amount of Hg that can be sorbed by the SAMMS (mg/g). Fitting by the least-squares method (Figure 2B) yielded values for K of 0.1758 L/g and for b of 476 mg/g in the experimental data using $HgCl_2$ and corresponding values of 0.1316 and 613 for the experiments using $Hg(NO_3)_2$.

The equilibrium isotherms suggest that Hg as $Hg(NO_3)_2$ is sorbed to a greater extent on the SAMMS than Hg as $HgCl_2$ under the same experimental conditions (Figure 2). This might be the result of complexation by the ligand Cl^- when $HgCl_2$ is used as the Hg source. Mercury is weakly complexed with NO_3^-, which is negligible under the experimental conditions. Thus, Hg species can be considered to be mostly Hg^{2+} or $HgOH^+$ in the experiments using $Hg(NO_3)_2$ as the Hg source. However, Hg differs from the other heavy metals in that it is more prone to form complexes (e.g., $HgCl_2°$) with chloride (17–20). The complexation results in a decrease in the concentration of free Hg species and thus a decrease in the concentration of $HgOH^+$, which subsequently decreases the sorption of Hg on the SAMMS surface. This chloride effect is consistent with other reports that chloride decreases the adsorption of Hg (17, 20, 21).

Stability of Hg-Laden SAMMS

Table 2 shows the analytical results of duplicate hydrothermal leaching tests of Hg-laden SAMMS under the conditions of 70°C and RT. The tests at 70°C had total Hg

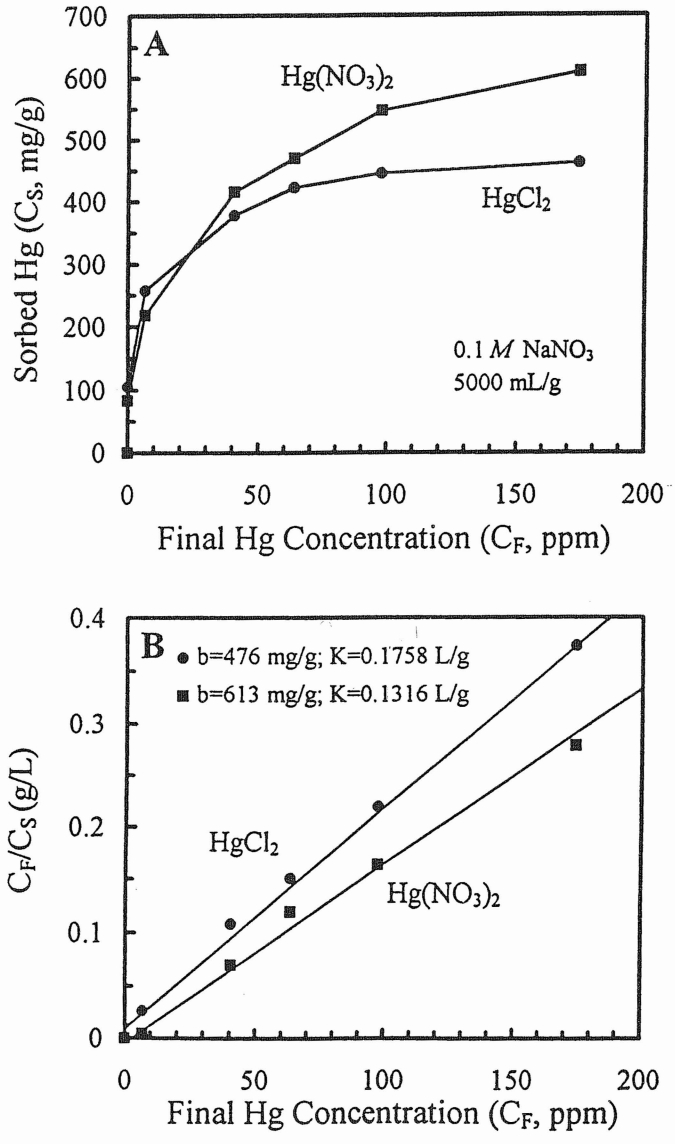

FIGURE 2. Langmuir sorption isotherms of Hg on SAMMS using $Hg(NO_3)_2$ and $HgCl_2$ as Hg sources (A) and their linear fittings (B) after the transformation by the Langmuir equation (2). K = sorption constant; b = maximum sorption capacity.

TABLE 2. MERCURY CONCENTRATIONS IN LEACHATES OF HYDROTHERMAL LEACHING EXPERIMENTS

	Total Hg (ppm)	Covalent Bound Hg (ppm)
SAMMS 1 (70°C)	12.7	2.15
SAMMS 2 (70°C)	13.0	2.45
SAMMS 3 (RT)	10.5	*NA*
SAMMS 4 (RT)	10.6	*NA*

NA = Not applicable.

concentrations of 12.7 and 13.0 ppm in their respective leachates, while the solutions from the experiments at RT contained 10.5 and 10.6 ppm Hg. The experiments performed at RT suggest that the Hg-laden SAMMS used for the tests was not washed thoroughly and some Hg simply might have been loosely adsorbed on the SAMMS surface. Assuming that the loosely adsorbed Hg was not covalently bound to the SAMMS surface, the experiments conducted at 70°C indicate that the release of Hg resulting from hydrolysis of the Hg-laden SAMMS at elevated temperature was limited if not negligible. A complete release of the Hg from the 0.05 g of Hg-laden SAMMS into 50 mL deionized water would result in a Hg concentration of 335 mg/L. The Hg release resulting from heating to 70°C accounts for changes of Hg concentration of 2.15 and 2.45 ppm in the tests (Table 2). The experimental results suggest a high stability of the Hg-laden SAMMS in aqueous solution at 70°C. Previous studies using nuclear magnetic resonance (NMR) also show that there was no Hg loss and no change in the chemical nature of the Hg-laden SAMMS after heating in the air at 70°C for 24 h (7).

The TCLP is widely used in the United States to determine whether a waste is hazardous or whether a treated waste meets the treatment standards for land disposal. The procedure was designed to study the mobility of hazardous substances and thus must be considered in the development of a treatment technology. Feng et al. (7) reported that the Hg-laden SAMMS could successfully pass the TCLP evaluation. The Hg-laden SAMMS, therefore, can be expected to have long-term durability as a permanent waste for disposal. The strong binding between Hg and the SAMMS and the physical nature of mesoporous oxides also suggest a long-term stability of the Hg-laden SAMMS. The covalent binding between Hg and the SAMMS possesses good resistance to ion exchange, oxidation, and hydrolysis. The uniform and small pore size of the mesoporous silica can prevent microbes from solubilizing the bound mercury, thus decreasing the mobility of the bound Hg. Thus, the SAMMS technology is distinctive because no secondary treatment of the Hg-laden SAMMS is required.

CONCLUSIONS

The SAMMS technology was extremely effective in separating and immobilizing Hg from aqueous solutions. The high surface area of the mesoporous silica and the

covalent binding between the thiol (-SH) group in SAMMS and Hg in solution provide SAMMS with distinctive advantages over existing technologies. The sorption kinetics was rapid as compared with the commercial organic resin, Duolite™ GT-73. The SAMMS can reduce Hg concentrations from the ppm to the ppb level in the order of minutes. The selectivity of SAMMS for Hg was very high, enabling it to reduce the Hg concentration to less than 10 ppt. The SAMMS had a large loading capacity for Hg, which could be up to approximately 613 mg of Hg per gram of SAMMS. The Hg-laden SAMMS was able to pass regulatory tests (e.g., TCLP) and had durable chemical stability. Thus, it requires no secondary treatment for disposal.

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