Novel Nanoporous Sorbents for Removal of Mercury

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Introduction

There is a significant need for a technology to effectively remove mercury 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). During the last few years, we have designed and developed a new class of high-performance sorbent material for removing toxic constituents such as mercury from water and waste water. This novel material is created from a combination of a synthetic nanoporous ceramic substrate that had a specifically tailored pore size (~6.5nm) and very high surface areas (~900 m^2/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. Detailed descriptions of the synthesis, fabrication, and adsorptive properties of these novel materials have been published previously[1-3]. We conducted a series of tests to evaluate the effectiveness of a synthetic novel sorbent for removing mercury from coal-fired power plant effluents.

Experimental

The novel substrates were prepared *via* a surfactant templated synthesis. The resulting siliceous structure was calcined to obtain a ceramic substrate with average pore size of 6.5 nm. Mercury is a very soft Lewis acid, and hence, both kinetically and thermodynamically "prefers" to undergo reaction with soft bases, such as thiols. Therefore, we functionalized the pores of the substrate with self-assembled monolayers of alkylthiols (Figure 1). The resulting mercury-specific adsorbent (thiol-SAMMS – thiol Self Assembled Monolayers on Mesoporous Silica) was tested to evaluate its adsorption capacity, specificity, and kinetics. Tests were conducted to: 1) evaluate the adsorption performance over a range of pH and ionic strengths of contacting solution, 2) determine the effects of equimolar concentrations competing cations on Hg-adsorption at two different pH values and, 3) assess the leachability of mercury-loaded SAMMS material using the Toxicity Characteristics Leaching Procedure (TCLP) of U. S. Environmental Protection Agency (USEPA).

A bench-scale treatability test was conducted to evaluate the mercury adsorption performance of thiol-SAMMS from a condensate waste stream. The principal dissolved components in this alkaline waste stream (pH: 8.5) consisted of mainly sodium borate (~30 mM), and sodium fluoride (~9 mM) with minor concentrations of sodium chloride(~3 mM), sodium nitrite (~0.9mM), sodium sulfate (~0.8mM), sodium nitrate (~0.6mM) and sodium iodide (~0.2 mM),. The mercury concentration in solution was measured to be 4.64 mg/L. Trace concentrations (<2 mg/L) of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mo, Ni, PO_4, Pb and Zn were also detected in this waste stream. To test the effectiveness of thiol-SAMMS in adsorbing mercury from this complexing matrix, thiol-SAMMS (Solution to solid ratio 1250 ml/g) was reacted with the waste solution for 8 hours.

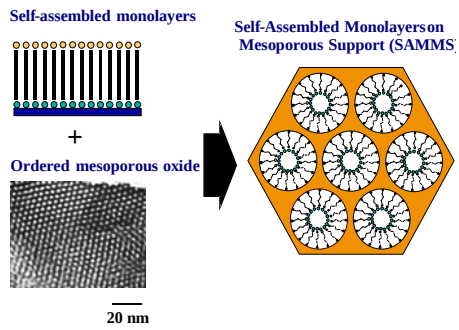

Figure 1. Technological basis of novel nanoporous sorbents

Results and Discussion

Adsorption of mercury by thiol-SAMMS showed a good fit to Langmuir isotherm (Figure 2). From the fitting parameters, the adsorption maximum was calculated to be 625 mg of Hg/g of sorbent, and the Langmuir constant was estimated to be 0.107 l/mg.

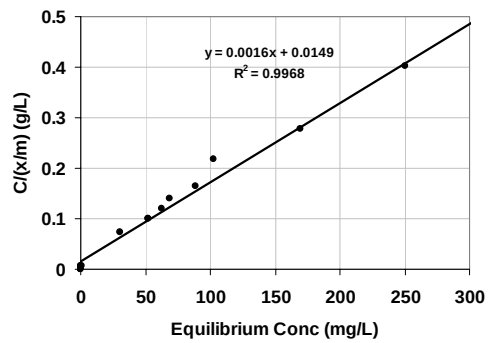

Figure 2. Langmuir Isotherm for Hg Adsorption by thiol-SAMMS

The kinetic data indicated (Figure 3) that adsorption was relatively rapid with ~99% dissolved mercury being adsorbed within the initial five minutes. Results of the TCLP (Toxicity Characteristics Leaching Procedure) tests indicated that Hg-adsorbed by the thiol-SAMMS was highly resistant to leaching (Figure 4).

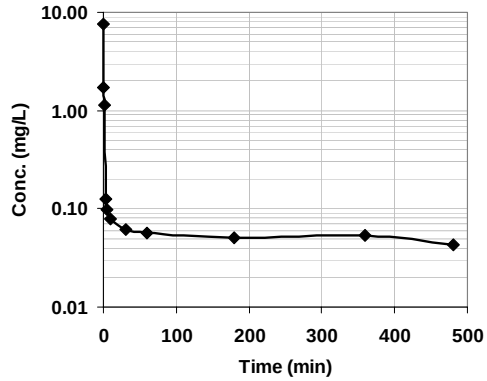

Figure 3. Kinetics of Hg Adsorption by thiol-SAMMS

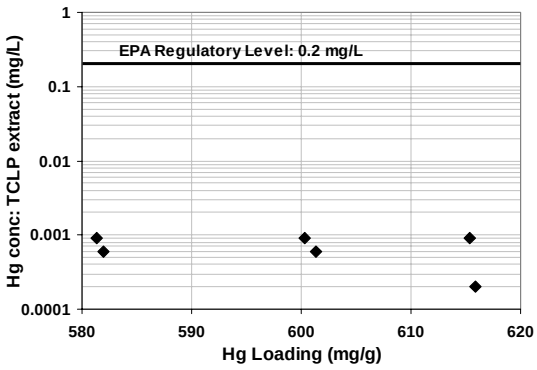

Figure 4. Leach Resistance of Hg-loaded thiol-SAMMS

Variation in pH or ionic strength did not significantly affect the Hg-adsorption affinity of thiol-SAMMS substrate (Table 1). The data showed (Table 2) that the presence of equimolar concentrations of competing cations at both pH values (4 and 7) did not significantly affect the specific adsorption of mercury. These data confirmed that mercury-thiol interaction being a soft acid-base interaction is both kinetically and thermodynamically a preferred reaction thus would not be significantly affected by pH, and the presence of competing cations in solution.

Table 1. Effect of pH and Ionic Strength

pH	K_d (ml/g)	$NaNO_3$(M)	K_d (ml/g)
2	$9.9x10^5$	0.0	$5.5x10^7$
3	$1.4x10^6$	0.1	$3.5x10^7$
4	$1.7x10^7$	0.3	$3.3x10^7$
5	$1.7x10^7$	0.6	$2.4x10^7$
7	$3.9x10^7$	2.0	$5.5x10^7$
8	$4.8x10^7$	3.0	$5.3x10^7$
10	$7.6x10^6$	4.0	$5.6x10^7$

Table 2. Effect of pH and Competing Cations

pH	Cations	K_d (ml/g)
4	Na	$1.5x10^7$
4	Ca, Cu(II), Fe(II), Pb	$1.0x10^7$
4	Ca, Cd, Cu(II), Fe(II), Ni, Pb, Zn	$1.0x10^7$
7	Na	$3.9x10^7$
7	Ca, Cu(II), Fe(II), Pb	$1.1x10^7$
7	Ca, Cd, Cu(II), Fe(II), Ni, Pb, Zn	$4.5x10^7$

The data from the bench scale test of the condensate waste stream indicated that thiol-SAMMS had adsorbed ~98.9% of the mercury initially present in this solution (residual mercury concentration 0.052 mg/L). This solution contained ~0.2 mM of iodide, a strong mercury complexing ligand and the speciation calculations indicated that all the soluble mercury existed in the form of iodide complexes (HgI_2^0: ~52%; HgI_3^-: ~47%, and HgI_4^{2-}: ~1%). These results confirmed previous observation[4] that thiol-SAMMS can effectively remove iodide-complexed mercury from solutions.

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References

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