

# Functionalized Nanoporous Ceramic Sorbents for Removal of Mercury And Other Contaminants

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## ABSTRACT

A new class of high-performance nanoporous sorbents has been developed for heavy metal removal that overcomes the deficiencies of existing technologies. These novel materials are created from a combination of synthetic nanoporous ceramic substrates that have specifically tailored pore sizes (2 to 10 nm) and very high surface areas (~1000 m<sup>2</sup>/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. These sorbents known as SAMMS™ (Self-Assembled Monolayers on Mesoporous Silica) are hybrids of two frontiers in materials science: molecular self-assembly techniques and nanoporous materials. One form of SAMMS™ containing monolayers of mercaptopropyl-trimethoxy silane has shown exceptional sorptive properties for mercury and other soft cations such as silver, cadmium, and lead. Another form of SAMMS™ with a functional monolayer consisting of ethylenediamine-Cu(II) complex (Cu-EDA) specifically adsorbs tetrahedral oxyanions such as arsenate, selenate, molybdate, chromate and pertechnetate even in the presence of high concentrations of sulfate. Separation of actinides can be addressed by SAMMS™ material synthesized with a set of monolayer functionalities consisting of hydroxypyridinones, acetamide and propinamide phosphonates. These nanoporous sorbents offer a better choice for efficient and cost-effective removal of contaminants from diverse waste streams.

**Keywords:** nanoporous sorbent, self-assembled monolayers, heavy metals, oxyanions, radionuclides

## 1 INTRODUCTION

Silica based nanoporous materials using liquid crystal templating was achieved about a decade ago [1, 2]. This has led to a number of applications of these nanoporous materials in diverse fields such as catalysis, sensor technology, and sorbents. Due to their relatively high surface areas (~500 – 1000 m<sup>2</sup>/g), nanoporous materials as sorbents offer a significant advantage over conventional sorbents, and to be effective in this role, it is necessary to functionalize the pore surfaces of these materials..

We have developed a method to activate the pore surfaces of the silica based nanoporous materials so that

these materials could be used as effective sorbents. This process consists of synthesizing within pores, self-assembled monolayers of adsorptive functional groups that are selected to specifically adsorb specific groups of contaminants. 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 group and a hydrophobic tail group adsorb onto a substrate or an interface as closely packed monolayers. 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 the molecular bonding between the organic molecules and the metals on the other. For instance, populating the head group with alkylthiols (which are well-known to have a high affinity for various soft heavy metals, including mercury) results in a functional monolayer that specifically adsorbs heavy metals such as, Hg, Ag, Cd, Cu, and Pb). If the head group consists of Cu-ethylenediamine complex (Cu-EDA) the monolayer will with high specificity adsorb oxyanions (As, Cr, Se, Mo). Additional monolayers with head groups we have designed include acetamide (APH) and propinamide (PPH) phosphonates for binding actinides (Am, Pu, U, Th). The functionalized monolayer and substrate composite was designated as SAMMS™ (Self-Assembled Monolayers on Mesoporous Silica). Detailed description of the functionalization techniques have been published previously [3-5]. Various self-assembled monolayer functionalities and the contaminants they were designed to target are shown in Table 1.

SAMMS™ Type	Contaminant
thiol	Ag, Cu, Cd, Hg, Pb
Cu-EDA	As, Cr, Se, Mo, <sup>99</sup> Tc
APH, PPH	<sup>241</sup> Am, <sup>237</sup> Np, <sup>239</sup> Pu, <sup>238</sup> U

Table 1. SAMMS™ Technology developed for Contaminant Removal

## 2 ADSORPTION DATA

### 2.1 Thiol-SAMMS™

Heavy metal adsorptive properties of thiol-SAMMS was tested by contacting known quantities of sorbent with a fixed volume of 0.1M NaNO<sub>3</sub> solution containing of the metal of interest (Ag, Cd, Cu, Hg Pb). The initial concentrations of these metals ranged from 0.05 to 12.5 meq/L and the solution to sorbent ratio in these experiments ranged from ~200 – 5000 ml/g. The suspensions were continually shaken and allowed to react under ambient temperature conditions (~25 °C) for approximately 8 hours. Next, the sorbent and the contact solutions were separated by filtration and the residual metal concentrations in aliquots were measured by using inductively-coupled plasma mass spectrometry (ICP-MS).

The data from the adsorption experiments indicated that thiol-SAMMS adsorbed the heavy metals with significant affinity (Table 2). The predicted adsorption maxima were 0.56, 0.72, 1.27, 4.11 and 6.37 meq/g for Cu, Pb, Cd, Ag, and Hg respectively. The calculated distribution coefficients were  $4.6 \times 10^1 - 1.8 \times 10^5$ ,  $2.2 \times 10^2 - 8.6 \times 10^3$ ,  $2.2 \times 10^2 - 1.9 \times 10^4$ ,  $1.2 \times 10^3 - 8.7 \times 10^5$ , and  $1 \times 10^3 - 3.5 \times 10^8$  ml/g for Cu, Pb, Cd, Ag, and Hg respectively. Such selectivity and affinity in binding these heavy metals by thiol-SAMMS can be explained on the basis of the hard and soft acid base principle (HSAB) [6-8] which predicts that the degree of cation softness directly correlates with the observed strength of interaction with soft base functionalities such as thiols (-SH groups). According to the HSAB principle, soft cations and anions possess relatively large ionic size, low electronegativity, and high polarizability (highly deformable bonding electron orbitals) therefore, mutually form strong covalent bonds. The order of adsorption maxima observed in this experiment appears to reflect the order of softness calculated by Misono et al [9] for these heavy metals.

Heavy Metal	Adsorption Max (meq/g)	K <sub>d</sub> (ml/g)
Ag	4.11	$1.2 \times 10^3 - 8.7 \times 10^5$
Cd	1.27	$2.2 \times 10^2 - 1.9 \times 10^4$
Cu	0.56	$4.6 \times 10^1 - 1.8 \times 10^5$
Hg	6.37	$1.0 \times 10^3 - 3.5 \times 10^8$
Pb	0.72	$2.2 \times 10^2 - 8.6 \times 10^3$

Table 2. Heavy Metal adsorption characteristics of thiol-SAMMS

### 2.2 Cu-EDA SAMMS™

Oxyanion adsorption characteristics of Cu-EDA SAMMS™ was evaluated by contacting the sorbent with 3 meq/L of Na<sub>2</sub>SO<sub>4</sub> solution containing either chromate (~0.02 – 18 meq/l) or arsenate (~0.01 – 29 meq/l) ions.

Solution to sorbent ratio in these experiments ranged from 100 – 500 ml/g. After 12 hours of contact, filtered aliquots of solution were analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES).

Results of the arsenate and chromate adsorption tests indicated that Cu-EDA SAMMS very effectively adsorbed both these oxyanions from Na<sub>2</sub>SO<sub>4</sub> solution. The predicted adsorption maxima from the Langmuirian fit to the data were 2.13 and 2.08 meq/g for arsenate (HAsO<sub>4</sub>) and chromate (CrO<sub>4</sub>) respectively. The calculated distribution coefficients were  $2.4 \times 10^2 - 1.0 \times 10^4$  and  $1.7 \times 10^2 - 1.0 \times 10^6$  ml/g for arsenate and chromate respectively. The bonding mechanism of these oxyanions was studied by Kelly et al [10,11] using X-ray Adsorption Fine Spectroscopy (XAFS) which indicated that bonding was monodentate in nature. The copper ion was bonded directly to the oxyanion by a shared oxygen. The adsorption process changed the coordination of copper from octahedral to trigonal bipyramidal geometry. The bonding did not alter the tetrahedral symmetry of HAsO<sub>4</sub> ion whereas, the symmetry of the CrO<sub>4</sub> ion was distorted with two short and two long Cr-O bond distances.

### 2.3 Acetamide- Propinamide Phosphonate SAMMS

The actinide-specific APH- and PPH-SAMMS™ were tested by contacting 100 mg quantities of each these sorbents with 10 mL portions of solutions containing  $2 \times 10^6$  counts per minute (CPM)/l of Pu(IV) in a matrix of acidified (pH=1) 1M NaNO<sub>3</sub> with separately spiked (0.01M) Pu-complexing ligands such as, phosphate, sulfate, ethylenediaminetetraacetate (EDTA), and citrate. After 1-4 hours of reaction, the solution was separated by filtration, mixed with Ultima Gold™ scintillation cocktail and the residual alpha activity of Pu(IV) was measured by using a liquid scintillation counter (2550 TR/AB Packard Instruments, Meriden, Conn).

Plutonium adsorption data (Table 3) indicated that both APH and PPH SAMMS™ adsorbed this actinide with high specificity. However, on average, APH SAMMS performed slightly better in adsorbing Pu(IV) from solution. In this experiment, the presence of complexants with differing chelating strengths did not significantly affect Pu(IV) adsorption by these nanoporous sorbents. Considering that the complexation constants of Pu(IV) with these ligands vary in the order EDTA>Citrate>phosphate >>sulfate>nitrate[12] very high adsorption affinity shown by these sorbents indicate that the CMPO ligand (APH and PPH) functionality based adsorption substrates are capable of chelating Pu(IV) much more strongly than these ligands. Additionally, the APH SAMMS has been shown to adsorb Pu(IV) very rapidly with bulk of the sorbate removed from solution under one minute [13].

Ligand	APH SAMMS	PPH SAMMS
	-----K <sub>d</sub> (ml/g)-----	
Nitrate	2.12 x 10 <sup>4</sup>	1.58 x 10 <sup>4</sup>
Nitrate+Phosphate	2.04 x 10 <sup>4</sup>	1.75 x 10 <sup>4</sup>
Nitrate+Sulfate	1.98 x 10 <sup>4</sup>	1.82 x 10 <sup>4</sup>
Nitrate+EDTA	2.05 x 10 <sup>4</sup>	1.56 x 10 <sup>4</sup>
Nitrate+Citrate	2.31 x 10 <sup>4</sup>	1.87 x 10 <sup>4</sup>

Table 3. Adsorption of Pu(IV) by APH- and PPH-SAMMS

### 3. SUMMARY AND CONCLUSIONS

Tests conducted on a new class of functionalized nanoporous materials showed that these are very effective in removing heavy metals, oxyanion and radionuclide contaminants from aqueous waste streams. The thiol-functionalized SAMMS<sup>TM</sup> designed for heavy metal removal adsorbed 0.56 to 6.36 meq/g of Ag, Cd, Cu, Hg and Pb with very high selectivity (K<sub>d</sub> 4.6 x 10<sup>6</sup> to 3.5 x 10<sup>8</sup> ml/g).

Sorption tests conducted on Cu-EDA SAMMS<sup>TM</sup> showed that this material very effectively adsorbed arsenate and chromate with loading approaching ~2.1 meq/g with distribution coefficient values ranging from 1.7 x 10<sup>2</sup> to 1.0 x 10<sup>6</sup> ml/g.

Other forms of SAMMS<sup>TM</sup> (APH and PPH) developed for specifically adsorbing radionuclides indicated that they were quite effective in removing Pu(IV) from solutions containing various complexing ligands such as, EDTA, citrate, phosphate, sulfate, and nitrate. Distribution coefficients as high as 2 x 10<sup>4</sup> ml/g indicated that these nanoporous substrates are very effective scavengers for actinides such as Pu.

Self-assembled monolayers of selected functionalities on nanoporous silica substrates can achieve very high contaminant loadings with relatively high specificities. These novel class of sorbent materials show great promise for effective removal of wide variety of targeted contaminants from aqueous waste streams.

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