New functional materials for heavy metal sorption: "Supramolecular" attachment of thiols to mesoporous silica substrates

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A new class of sorbent material, which exhibits exceptional metal capture from contaminated natural water, features aromatic thiol ligands reversibly bound to functionalized mesoporous silica through non-covalent interactions and have the potential of being regenerable.

Access to sustainable, clean drinking water is an increasing concern as the Earth's human population continues its steady growth.[1] Degrading water quality in both industrialized and non-industrialized nations has the potential to cause great economic strain on the world's governing bodies.[2] At the same time, this offers a challenge to researchers to discover new, functional, designer materials that have high uptake capacities and selectivity for environmental contaminants.[3] The need to develop inexpensive and efficient water purification media is a high priority.

Current filter media typically consist of granular activated carbon (GAC) or a hybrid material that combines an inorganic oxide such as gamma alumina to achieve satisfactory water purification. This type of filter medium, although common and inexpensive, offers limited uptake potential. Additionally, spent media must be disposed of properly to prevent it from conceivably becoming a source of contamination due to leaching over time. An alternative to "one-shot" filters is the implementation of renewable media capable of many purification cycles before fouling.[4,5] One such approach is described here with the technique of non-covalent absorption of organothiol ligands onto self-assembled monolayers on mesoporous supports (SAMMS™).[6,7] Functionalized mesoporous supports have been found to be excellent sorbent materials, capable of being chemically modified with reactive head groups for toxic metal, metalloid and oxyanion uptake as well as radioactive species.[8,9] One particular silica-based support, MCM-41, has garnered much attention due to its controllable honeycomb-like porosity, structural integrity, chemical resistivity and high surface area, approaching 1000 m^2 g^{-1}.[10] A variety of commercially available and synthetically accessible functionalized organosilanes can be affixed inside the pores of the silica support as self-assembled monolayers. The result is a dense population of chelating sites which can achieve exceptionally high uptake levels of target species. It was recognized that phenyl monolayers, in which the aromatic rings were rigidly held upright and perpendicular to the surface, were well suited, both sterically and electronically, to serve as hosts to other functionalized arenes. This approach was envisioned not only to be a very versatile and easy functionalization strategy, but also one that would readily provide for "refreshable" functionalization without the need for acid stripping.[5] Herein we describe the functionalization of MCM-41 with phenyl monolayers at various densities to provide a hydrophobic scaffolding for non-covalently bound benzylmercaptan (BM), 1,3- and 1,4-bis(mercaptomethyl)-benzenes (1,3- and 1,4-BMMB, respectively) for use in heavy metal uptake from native waters (Fig. 1).

Thiol-SAMMS derived from covalent attachment of (tris(methoxy)mercaptopropylsilane) to MCM-41 yielding high chelation site densities, have shown excellent uptake levels of soft and moderately soft metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+}, and Ag^{+}.[9] We have extended the breadth of thiol-SAMMS style sorbent materials with this research to include non-covalently bound mono- and dithiol aryl ligands attached by relatively weak, reversible π-stacking interactions. Remarkably, these materials exhibit comparable metal ion uptake levels to the covalently bound thiol-SAMMS. MCM-41 was functionalized at different surface loading levels by first hydrating the silica surface with a toluene–water mixture (equal to two monolayers of water based on total surface area) followed by addition of trichlorophenylsilane and an overnight stir at room temperature.[11, 12] Phenyl coverage was determined by gravimetric analysis, taking the change in mass and dividing by the total surface area to give

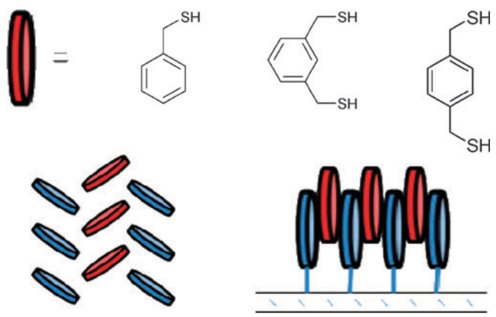

Fig. 1 (top) Graphical representation of organothiol ligands benzylmercaptan (BM), 1,3-bis(mercaptomethyl)benzene (1,3-BMMB), and 1,4-bis(mercaptomethyl)benzene (1,4-BMMB), (bottom) cartoon representation of functionalized mesoporous silica monolayer (blue disks) and chemisorbed ligands (red disk) in idealized herringbone (left) and offset (right) orientations.

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an average distribution of ligand which ranged from 0.01 molecules nm^{-2} (sparsely covered surface) to 3.1 molecules nm^{-2} (near maximum achievable loading accessible by this technique).[13] Sparsely covered substrates presumably contain island domains rather than complete surface coverage due to the limited chlorosilane present in the reaction mixture.

A comparison of 1,4-BMMB physisorbed onto native MCM-41 *versus* the phenyl modified support (phenyl-SAMMS) containing chemisorbed 1,4-BMMB at two different ligand loading levels revealed a significantly different burn off rate by TGA after the initial water desorption.[14] The result is a relatively rapid weight loss starting around 235 °C and ending near 255 °C (Fig. 2, dashed lines) for the physisorbed ligand. 1,4-BMMB ligand desorption from the phenyl monolayer stabilized silica occurs at a slightly elevated temperature compared to the non-stabilized silica and continues over roughly 200 °C to around 350 °C, verified by the continued detection of SO^+ (47.9 m/z) and SO_2^+ (63.8 m/z) by mass spectrometry.[15] The loss of the phenyl monolayer was observed above 350 °C and continued to 600 °C, also monitored by EI-MS with ions detected at 49.9, 50.8, 51.8 and 78.2 m/z which correspond to $C_6H_6^+$ fragmentation typical of this type of mass analyzer. The extended burn off range of 1,4-BMMB can be accounted for by an increase in stabilization of the chemisorbed arylthiol ligands afforded by the weak, reversible interactions between phenyl monolayer and adsorbed ligand. Benzylmercaptan (BM) was also found to be stabilized by the phenyl monolayer as indicated by TGA (data not shown) however, a strong, thiol odor emanated from this material making it unsuitable for use in filtration applications. Additionally, uptake levels for BM were less than that of 1,3- and 1,4-BMMB as expected due to the presence of a single thiol group. FT-IR provided useful analysis of the surface makeup by comparing relative intensities of prominent peaks between samples. The thiol S–H and C–S stretching, 2545 and 669 cm^{-1}, respectively, was normalized to the aryl C–H (2926 and 698) and C=C (1595, 1512 and 1431 cm^{-1}) stretching to verify loading of both monolayer and adsorbed ligand. Chemisorbed 1,4-BMMB sorbent material with bound Pb^{2+} or Hg^{2+} lacked any S–H stretching as expected. In addition, powder XRD revealed a dominant (100) peak at 2.11° but lacked higher angle peaks for all substrates. It has been reported that a decrease in peak intensity is directly related to the extent of modification of the pore with organics. We observed a similar decrease in the (100) peak intensity consistent with the chemisorption of 1,4-BMMB on to phenyl-SAMMS.[16] A plot of log K_d values for phenyl-SAMMS loaded at 3.1 molecules nm^{-2} containing chemisorbed 1,4-BMMB loaded at either 2 : 1 (low) or 1 : 1 (high) shows similar capture levels with the covalently attached thiol-SAMMS in Hanford well water matrix spiked with 500 ppb Hg^{2+}, Pb^{2+}, Cd^{2+}, and Ag^+ ions (Fig. 3, top).[17] 1,3- and 1,4-BMMB exhibited similar uptake levels at near equivalent loadings (Fig. 3, bottom), an unexpected result due to the assumed herringbone arrangement between the phenyl monolayer and the chemisorbed ligands, which would result in at least one thiol group of 1,4-BMMB being buried in the monolayer to maximize edge to edge contacts (Fig. 4, right).[19] This appears not to be the case due to the similar uptake levels between 1,3- and 1,4-BMMB with lower levels for BM containing only one reactive thiol under similar loadings. A possible explanation is that the BMMB ligands are only partially intercalated into the phenyl monolayer in an offset stacking[20] resulting in sufficient accessibility by the metal ions to the bulk of the thiol head groups (Fig. 4, left and middle) or that the covalently attached phenyl monolayer exists in a disordered herringbone configuration which can accommodate further π-stacking from chemisorbed arylthiol ligands.[21] One interesting observation is that as 1,4-BMMB loading increases, uptake decreases for Hg^{2+}, Cd^{2+}, and Ag^+ but not for Pb^{2+}. This may be due to the thiol sites becoming buried in the monolayer as loading densities increase, forcing rearrangement of the rings to maximize contacts. It is known from previous studies in our group that densely packed thiol head groups of thiol-SAMMS material are shared by the same metal ion resulting in ML$_n$ species where $n > 1$.[7] This desire to maximize metal–thiol contacts may manipulate the weakly bound chemisorbed ligands to adopt a more ideal geometry for binding at the various loadings investigated. In either case, the metal affinity levels of the chemisorbed BMMB phenyl-SAMMS is near equal to that of the covalently bound

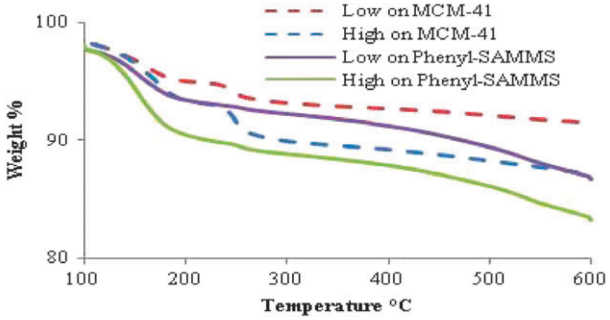

Fig. 2 TGA comparison of various chemisorbed loading densities of 1,4-BMMB on phenyl functionalized MCM-41 (solid lines) *versus* physisorbed 1,4-BMMB on native MCM-41 silica (dashed lines).

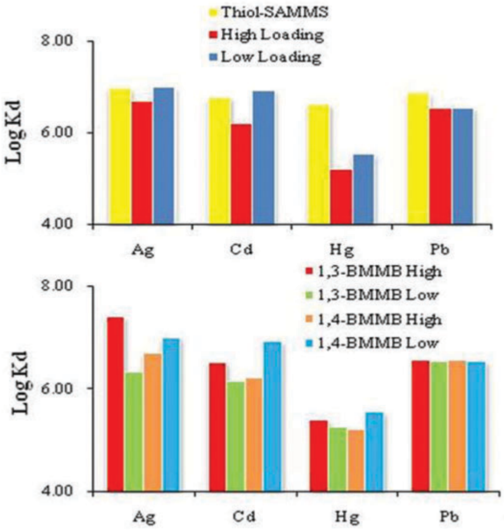

Fig. 3 log K_d values of thiol-SAMMS *versus* 1-4-BMMB at two different loading levels (top). Comparison of 1,3- and 1,4-BMMB at similar loading levels (bottom) in Hanford well water.[18]

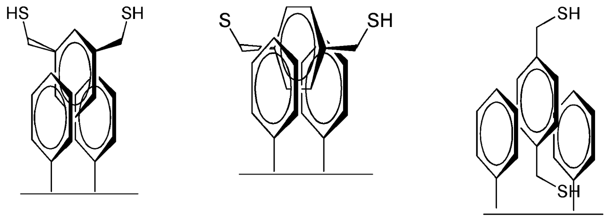

Fig. 4 An idealized model showing possible orientations of the chemisorbed ligands onto the phenyl monolayer with both thiols accessible (left and middle) and 1,4-BMMB with one thiol buried (right).

thiol-SAMMS, which has been shown to have affinity levels for heavy metal ions one to three orders of magnitude greater than commercially available thiol-based resins such as GT-73.[22]

The effects of density of the covalently bound phenyl layer were also probed by varying the loading from 0.01 phenyl molecules nm^{-2} to as high as 3.1 molecules nm^{-2} while maintaining 1,3- and 1,4-BMMB loading levels equal to previous tests. Surprisingly, the sparsely populated phenyl-SAMMS with chemisorbed BMMB performed equal to that of material of higher phenyl monolayer density. The exact nature of the interaction between the covalently attached phenyl ring and that of chemisorbed BMMB is not well understood at this time, but the bound phenyl ring of the monolayer appears to be capable of acting as a nucleation site resulting in BMMB anchoring to the surface in a stacked or offset manner to provide a surface rich in chelation sites capable of metal ion uptake—a feature lacking with the native silica and phenyl modified support.

In conclusion, the above described materials utilize weak interactions to reversibly bind aromatic molecules containing reactive head groups capable of selective capture of toxic metal ions from aqueous matrices at levels equal to covalently bound analogs. Numerous common organic solvents were screened for use as a means to rinse the captured metal from the sorbent. Both chloroform and pentane (to a lesser extent) were capable of removing Hg complexes resulting in regeneration of pristine phenyl-SAMMS. The ability to refresh or replace the surfaces of highly engineered sorbent support structures, such as mesoporous silica, could significantly increase the range of viable applications for these materials. These studies are ongoing with the potential outcome of producing regenerable filter media.

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