

# Trapping of arsenite by mercaptopropyl-functionalized mesostructured silica with a wormhole framework

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Thiol-functionalized mesostructured silica, prepared by direct assembly methods, is an effective trapping agent for the removal of arsenite from water.

Arsenic in naturally occurring form is found in soil, air and water. Of the two forms of inorganic arsenic found in ground water, namely, arsenite (As(III)) and arsenate (As(V)), arsenite is predominant. A variety of harmful health effects have been attributed to arsenic in drinking water.<sup>1</sup> Furthermore, arsenite is estimated to be 60 times more toxic than arsenate.<sup>2</sup> Current remediation techniques<sup>3</sup> (e.g., coagulation, nanofiltration, or ion-exchange) are effective only in removing arsenate, but not arsenite, in part, because arsenite is not anionic below pH 8.5 in aqueous solution. Thus, the common approach to the removal of arsenite from ground water anticipates oxidizing arsenite to arsenate.

Functionalized mesostructured materials have been examined as adsorbents for heavy metals, especially mercury.<sup>4-6</sup> These compounds have large surface areas, and tailorable mesopore sizes to facilitate access to complexing ligands immobilized on the pore walls. Current arsenic remediation efforts based on organo-functionalized mesostructures have focused on the trapping of arsenate.<sup>7-9</sup> One approach relies on the Lewis base properties of the anion and the formation of a complex with Lewis acid metal centers (i.e., copper(II) or iron(III)) immobilized in the pores of the mesostructure.<sup>8,9</sup> The second strategy is based on ion pairing between an onium ion immobilized on the pore walls and anionic arsenate.<sup>7</sup> However, neither binding mechanism is effective in trapping arsenite.

In light of the toxicity and prevalence of arsenite in ground water, our focus has been on designing a functionalized mesostructured silica for the direct trapping of arsenite, without the necessity of pre-oxidizing arsenite to arsenate. Trivalent arsenic is known to have an especially high affinity for binding to mercaptan groups.<sup>10</sup> Moreover, mercaptans are much more selective towards binding to arsenite than to arsenate.<sup>11</sup> Accordingly, we have examined the uptake of arsenite by mercaptopropyl-functionalized silica mesostructures.

The mesostructures of interest, denoted MP-HMS, have a wormhole framework structure and an anhydrous composition of  $(\text{SiO}_2)_{1-x}(\text{LSiO}_{1.5})_x$ , where L is a mercaptopropyl moiety and  $x$  is the mole fraction of framework silicon centers that have been functionalized. Compositions with  $x = 0.10$  to 0.50 were prepared by a one-pot, direct assembly process from tetraethylorthosilicate (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of a structure-directing amine surfactant (dodecylamine)

as the porogen in accord with a previously reported method,<sup>10</sup> except that the order of the addition of reagents differed with water being the last reagent added to the reaction mixture at 65 °C. The molar reaction stoichiometry employed was  $(1 - x)$  TEOS :  $x$  MPTMS : 0.22 DDA : 6.7 EtOH : 160 H<sub>2</sub>O. The direct assembly route was preferred over the more commonly used post synthesis grafting reaction between surface silanols and organo-functional silating agents. Direct assembly provides for a more homogenous distribution of organic ligands in the framework pores<sup>12</sup> and allows for better crosslinking of the organosilyl group into the framework walls.

Arsenite uptake curves were obtained by slurring a 200 mg quantity of MP-HMS with  $x = 0.10, 0.20, 0.30, 0.40,$  and 0.50 in 20 ml of water containing different initial concentrations of H<sub>3</sub>AsO<sub>3</sub> for a period of 20 h at room temperature. The standardized H<sub>3</sub>AsO<sub>3</sub> solution was adjusted to pH = 7.0 with 0.11 N sodium hydroxide before mixing with MP-HMS. The equilibrated suspensions were filtered to remove the MP-HMS trapping agent and the filtrate was analyzed for arsenite by titrimetric oxidation with an iodine–starch solution.<sup>13</sup>

As shown by the uptake curves in Fig. 1 the amount of arsenite adsorbed increased with increasing mercaptan functionalization. MP-HMS with  $x = 0.10$  and 0.20 quantitatively adsorb arsenite up to a SH/As ratio  $\geq 10$ . For  $x = 0.30$ , quantitative uptake of arsenite is observed up to SH/As  $\geq 6.7$ . Increasing the mercaptan loading still further to  $x = 0.40$  and 0.50 results in quantitative uptake up to SH/As  $\geq 5$  or up to 20% of the mercaptan centers. Therefore, the higher the thiol ligand loading the more efficient the

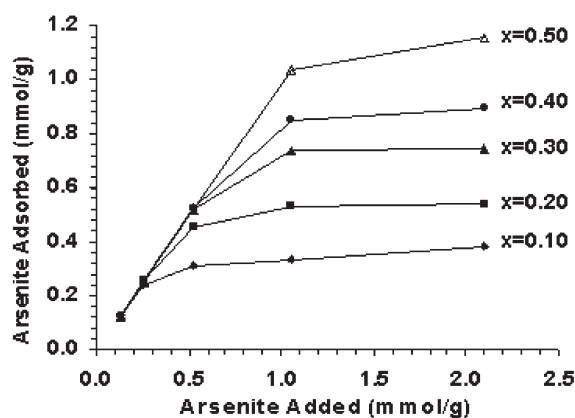


Fig. 1 Arsenite uptake curve for functionalized  $(\text{SiO}_2)_{1-x}(\text{LSiO}_{1.5})_x$  compositions (L = mercaptopropyl) with a wormhole framework structure, denoted MP-HMS.

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**Table 1** Adsorption of arsenite at pH = 7.0 by MP-HMS mesostructures with the anhydrous compositions of  $(\text{SiO}_2)_{1-x}(\text{LSiO}_{1.5})_x$ , L = mercaptopropyl

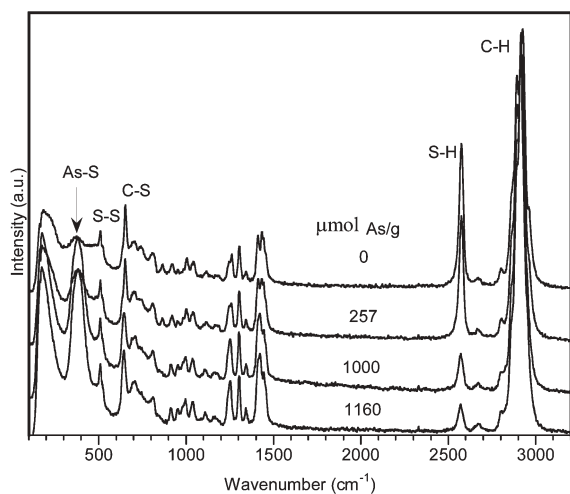
MP-HMS	Initial $\text{H}_3\text{AsO}_3$ (ppm)	Final $\text{H}_3\text{AsO}_3$ (ppm)	mmol SH $\text{g}^{-1a}$	$\mu\text{mol As g}^{-1}$ added	$\mu\text{mol As g}^{-1}$ adsorbed	% Removal
$x = 0.00$	323	313	0.0	525	$4.9 \times 10^{-4}$	1.8
$x = 0.10$	323	22.3	1.4	263	244	93
$x = 0.20$	323	6.1	2.6	263	259	98
$x = 0.30$	323	6.3	3.6	263	257	98
$x = 0.40$	323	6.1	4.4	263	252	96
$x = 0.50$	323	6.3	5.3	263	257	98

<sup>a</sup> mmol SH  $\text{g}^{-1}$  determined from  $^{29}\text{Si}$  MAS NMR.

uptake of arsenite. Efforts to prepare HMS mesostructures with  $x > 0.50$  resulted in unstructured products.

In order to further characterize arsenite uptake by MP-HMS derivatives, the initial concentration of arsenic in solution was held constant at 323 ppm while also keeping the weight of MP-HMS and the volume of solution constant. In this way only the ratio of As(III) to SH was varied, depending on the value of  $x$ . The results are summarized in Table 1. The non-functionalized HMS silica adsorbed a negligible amount of arsenite; indicating that the arsenite adsorption is due to bonding with the mercaptan. With an excess of 10 : 1 thiol to arsenite, 98% removal of arsenite from solution is achieved. This ligand to arsenic ratio suggests that only a fraction of the framework thiol sites are available for arsenite binding.

Raman spectroscopy was utilized in order to verify the binding of the arsenite to the mercaptan (Fig. 2). For the initial MP-HMS mesostructure, the mercaptan S–H stretch appears as a strong band at  $2560 \text{ cm}^{-1}$ .<sup>14,15</sup> A weak band at  $510 \text{ cm}^{-1}$  is assigned to a S–S stretch, indicating the presence of a small amount of disulfide due to air oxidation of adjacent thiol groups on the surface of the mesostructure.<sup>15</sup> The C–H stretch appears as a strong band at  $2900 \text{ cm}^{-1}$ .<sup>15</sup> For the mesostructures containing bound arsenite, an As–S stretch is present at  $\sim 375 \text{ cm}^{-1}$ .<sup>16,17</sup> Although a weak band in this region is present in the parent MP-HMS ( $x = 0.50$ ), the intensity grows in proportion to arsenite adsorption, indicating the presence of an As–S bond. Additionally, the decrease in



**Fig. 2** Raman spectra of functionalized  $(\text{SiO}_2)_{1-x}(\text{LSiO}_{1.5})_x$  compositions (L = mercaptopropyl,  $x = 0.50$ ) with a wormhole framework structure, denoted MP-HMS, after binding of arsenite at the  $\mu\text{mol As g}^{-1}$  levels shown. The spectra are offset on the y-axis for clarity.

intensity of the S–H stretch with arsenite adsorption, gives evidence for the binding of the arsenite directly to the thiol. No change in the S–S stretch was observed with arsenite loading, even though it has been reported that disulfides form stable complexes with arsenite.<sup>18</sup> In addition to the possible binding of arsenic to more than one sulfur, another potential explanation for the inability of all the mercaptan ligands to bind in a one to one manner with arsenic is related to the accessibility of the thiol groups. The Raman spectra do not rule out the possibility that arsenite might bind to special thiol sites in the silica framework. The limited presence of these “special” sites might be a reason that binding of one ligand to one arsenic is not observed.

The above results represent the first report of the remediation of arsenite by a mesostructured organo-silica. Arsenite concentration was reduced by up to 98% under batch equilibrium conditions. More efficient removal is anticipated under column processing conditions. Moreover, the adsorption of arsenite requires no additional processing steps, such as pre-oxidation of arsenite to arsenate or pH adjustment of the trapping agent. In addition, the trapping agent itself is prepared by a simple one-pot method that allows the surfactant template to be removed by Soxhlet extraction and recycled.

Although the arsenite adsorbed increases as the loading the thiol group increases, as expected, further information on the binding mechanism of the arsenite to mercaptan is needed. Also, column processing studies are needed to determine if the arsenite levels can be lowered to the EPA value of 10 ppb for drinking water.

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