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Selective adsorption of Hg^{2+} by thiol-functionalized nanoporous silica

Jennifer Brown,[a] **Louis Mercier***[a] **and Thomas J. Pinnavaia**[b]

[a] *Department of Chemistry and Biochemistry, Laurentian University, Sudbury, Ontario, Canada P3E 2C6. E-mail: lmercien@nickel.laurentian.ca*
[b] *Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824, USA*

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Thiol-functionalized nanostructured silicas with uniform porosities exhibit selective complexation affinity for Hg^{2+}, while other metal ions (Cd^{2+}, Pb^{2+}, Zn^{2+}, Co^{3+}, Fe^{3+}, Cu^{2+} and Ni^{2+}) have little or no binding ability with the adsorbents.

Effective metal ion adsorbents have been prepared by the immobilization of thiol ligands onto the surface of various substrates, including silica gel,[1,2] clays,[3,4] polymers[5] and, most recently, mesoporous silica.[6–8] The effectiveness of such materials in binding metal ions has been attributed to the complexation chemistry between the ligand and the metal, the specificity of a particular ligand towards target metal ions being the result of a conventional acid–base interaction between the two. Although some of these thiol-functionalized adsorbents can exhibit specific interactions with soft Lewis acids (such as Hg^{2+}, Cd^{2+}, Pb^{2+} and Ag^{+}),[1–4] the selectivities of these materials are usually unremarkable because many metals have the ability to bind with thiol ligands. In this study, we have prepared a series of nanostructured thiol-functionalized silica adsorbents with uniform porosity[9–11] and investigated their affinity for heavy metal ion binding.

Nanostructured adsorbents with variable loadings of thiol groups were prepared by stirring tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in 0.116 M *n*-octylamine solutions at room temperature [the molar composition of each mixture was 0.22 surfactant : $(1 - X)/100$ TEOS : $X/100$ MPTMS, where $X = 0$, 2.3, 4.5, 6.9 and 9.0]. After aging for 24 h, the resulting powders were filtered, air dried and washed by Soxhlet extraction over ethanol for 24 h. The materials were labeled as HMS ($X = 0$) and MP-HMS-*X*, where *X* represents the percentage of silicon atoms in the synthesis mixture present as MPTMS.

The physical and chemical properties of the functionalized silicas, shown in Table 1, were determined using X-ray diffraction (XRD), N_2 sorptometry and ^{29}Si MAS NMR. The single-reflection XRD powder patterns denoted disordered wormhole structures, with d_{100} values ranging from 2.9–3.4 nm. The N_2 adsorption isotherms showed that the adsorbents had very high surface areas and narrow Horvath–Kawazoe pore size distributions in the micropore range (< 2.0 nm). All of these characteristics are indicative of neutral–surfactant-assembled nanostructured silica frameworks with uniform porosities.[12–14]

Table 1 Physicochemical characteristics of the thiol-functionalized nanoporous adsorbents

Adsorbent	Lattice spacing/ nm	Surface area/ $m^2\ g^{-1}$	Pore diameter/ nm	SH content/ mmol g^{-1}	Hg^{2+} adsorption capacity/ mmol g^{-1}
HMS	3.15	1408	1.95	0	0
MP-HMS-2.3	3.13	1221	1.75	0.35	0.19
MP-HMS-4.5	2.96	1331	1.65	0.68	0.28
MP-HMS-6.9	3.13	1087	1.51	1.0	0.46
MP-HMS-9.0	3.34	1063	1.48	1.3	0.59

Resonances at δ −65 in the ^{29}Si MAS NMR spectra of the adsorbents demonstrated the incorporation of MPTMS within the material frameworks. By comparing the relative integral intensities of the MPTMS signals with respect to the total signal intensity,[9,11] we deduced that the amount of thiol groups incorporated in the materials (Table 1) corresponded within experimental uncertainty to the stoichiometry of the synthesis mixture. Consequently, the surface areas and pore sizes of the materials systematically decrease as a result of the increased coverage of thiol groups on the surface of the pore channels (Table 1). No evidence of thiol group oxidation was found in the materials, as evidenced by the detection of S–H stretching bands in their FTIR spectra (2580 cm^{-1}), and the presence of symmetric signals at δ −27 in their ^{13}C NMR spectra (characteristic of $R–CH_2–SH$ functions[7,9]).

The uptake of metal ions by the adsorbents were determined by titrating aqueous metal ion solutions into a slurry of each adsorbent, stirring for 24 h, and analyzing the supernatant solution for metal ion content using flame AAS (cold-vapour AAS for Hg). This process was repeated until no significant metal ion uptake by the materials was observed. Thus, each adsorbent was tested for their ability to adsorb Hg^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} from independent homoionic solutions at neutral pH. The adsorbents exhibited little or no affinity for these metals, with the exception of Hg^{2+}. The very efficient binding of Hg^{2+} ions reduced the metal concentrations to negligible levels (< 10 ppb) until saturation was reached [Fig. 1(a)]. The Hg^{2+} adsorption capacities of the materials systematically increased in proportion to the thiol group content in the materials [up to

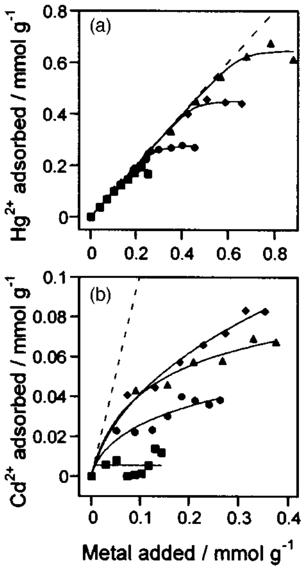

Fig. 1 Homoionic (a) Hg^{2+} and (b) Cd^{2+} uptake curves for MP-HMS-*X* adsorbents [$X = 2.3$(■), 4.5(●), 6.9(◆) and 9.0(▲)]. The *x*-axis denotes the total amount of metal added to the system per unit mass of adsorbent. The dashed lines are the unity slopes representing the theoretical total uptake of metal ions.

0.65 mmol g^{-1}, Fig. 1(a)]. Approximately one half of the incorporated thiol groups in each adsorbent is accessible for Hg^{2+} binding (Table 1). The constricted nature of the microporous channels most likely controls access of Hg^{2+} ions to the adsorbents' binding sites.[8,9] Multidentate SH binding with the Hg^{2+} ions may also contribute to the high S:Hg stoichiometry. Of the other metals studied, only Cd^{2+} demonstrated some interaction with the adsorbents [Fig. 1(b)]. As in the case of Hg^{2+}, a correlation between the thiol group content in the adsorbents and the Cd^{2+} loading is denoted, but saturation of the binding sites is reached at very low levels [$<<0.1$ mmol g^{-1}, Fig. 1(b)]. Significant residual concentrations of Cd^{2+} remained in the treated solutions, even at low metal concentrations [Fig. 1(b)]. The adsorbents thus demonstrate considerably weaker affinity for Cd^{2+} than for Hg^{2+}.

By the uptake process described above, the adsorbents were also used to treat a mixed metal solution containing nearly equimolar amounts of Cd^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, Co^{3+}, Fe^{3+}, Cu^{2+} and Ni^{2+}. The uptake of Hg^{2+} from this mixed metal ion solution was virtually identical to the uptake observed for the homoionic solutions [Fig. 1(a)]. Negligible adsorption of the other metals was observed. This demonstrates the remarkable selectivity of the nanoporous adsorbents for Hg^{2+} binding.

That Hg^{2+} ions exhibit high binding affinity towards the immobilized thiol groups is not unexpected. What is unique for the nanostructured adsorbents, however, is their extreme lack of affinity towards other d^{10} metal ions (Cd^{2+}, Zn^{2+} and Pb^{2+}) which usually bind strongly with these ligands (especially in the absence of other competing ions), as observed previously for thiol-functionalized silica gel[1] and montmorillonite.[3] We propose that, while Hg^{2+} has the ability to bind with the thiol groups lining the framework pore channels of the nanoporous adsorbents (representing the bulk of the adsorbent binding sites), the other metal ions are unable to bind to intraframework, complexing only with the comparatively low number of thiol groups present at the external surface of the adsorbent particles.

By comparing these results with those of other sorption studies on similar materials,[1–3] we infer that the uniform porosity of the nanostructured adsorbents is ultimately responsible for their selective adsorption behaviour. The inability of Cd^{2+}, Zn^{2+} and Pb^{2+} to bind to the thiol groups in the adsorbent pore channels may tentatively be explained by the thermodynamic inability of these ions to coordinate within the confined spaces of the pore channels. Using thermodynamic data tables[15] and the model reaction $H_2S + M^{2+} \longrightarrow MS + 2H^+$ to represent the metal ion binding process, we estimate the ΔG^0 value for the reaction in which M = Hg was calculated as -181.6 kJ mol^{-1}, while the free energies of the reactions in which M = Cu, Cd, Pb, Ni and Fe were -85.7, -45.3, -40.9, -0.5 and 11.9 kJ mol^{-1}, respectively. We postulate that the restricted volumes of the channels reduce the ΔS^0 values of the above reactions, resulting in positive (non-spontaneous) ΔG^0 values for most of the intraframework metal–ligand reactions. Only in the reaction with Hg^{2+} is the change in enthalpy (ΔH^0) sufficiently negative to overcome this unfavourable entropy effect and maintain reaction spontaneity. Further investigations are currently underway to verify this hypothesis and to better elucidate the factors involved in metal-ion binding to nanoporous adsorbents.

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