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H$_{2x}$Mn$_x$Sn$_{3\text{-}x}$S$_6$ (x $=$ 0.11–0.25): A Novel Reusable Sorbent for Highly Specific Mercury Capture Under Extreme pH Conditions

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The H$_{2x}$Mn$_x$Sn$_{3\text{-}x}$S$_6$ (x $=$ 0.11–0.25) is a new solid acid with a layered hydrogen metal sulfide (LHMS). It derives from K$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$ (x $=$ 0.5–0.95) (KMS-1) upon treating it with highly acidic solutions. We demonstrate that LHMS-1 has enormous affinity for the very soft metal ions such as Hg^{2+} and Ag$^+$ which occurs via a rapid ion exchange process. The tremendous affinity of LHMS-1 for Hg^{2+} is reflected in very high distribution coefficient K_d^{Hg} values ($>$10^6 mL g^{-1}). The large affinity and selectivity of LHMS-1 for Hg^{2+} persists in a very wide pH range (from less than zero to nine) and even in the presence of highly concentrated HCl and HNO$_3$ acids. LHMS-1 is significantly more selective for Hg^{2+} and Ag$^+$ than for the less soft cations Pb^{2+} and Cd^{2+}. The Hg^{2+} ions are immobilized in octahedral sites between the sulfide layers of the materials via Hg–S bonds as suggested by pair distribution function (PDF) analysis. LHMS-1 could decrease trace concentrations of Hg^{2+} (e.g. $<$100 ppb) to well below the acceptable limits for the drinking water in less than two min. Hg-laden LHMS-1 shows a remarkable hydrothermal stability and resistance in 6 M HCl solutions. LHMS-1 could be regenerated by treating Hg-loaded samples with 12 M HCl and re-used without loss of its initial exchange capacity.

1. Introduction

Mercuric (Hg^{2+}) and other soft heavy metal ions such as Cd^{2+} and Pb^{2+} represent major contaminants in natural water sources and industrial waste water and constitute a threat for humans and other species.[1] Conventional ion-exchangers such as zeolites[2] and clays[3] and adsorbents like activated carbon[4] generally have low selectivity and weak binding affinity for soft metal ions. Thiol-functionalized adsorbents, including clays,[5] resins,[6] organo-ceramics[7] and mesoporous silicates,[8,9] are considered the most effective sorbents for soft heavy metal ions and in particular for Hg^{2+}. In addition, mesoporous carbon materials with thiopyrene

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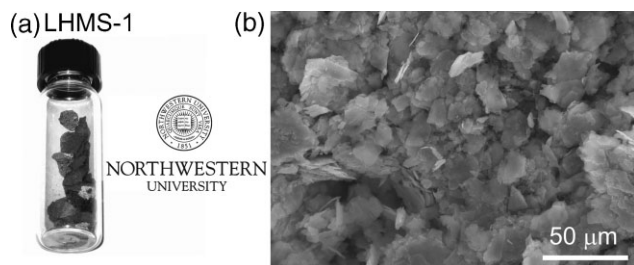E-mail: m-kanatzidis@northwestern.edu
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functional groups were proven to be excellent sorbents for mercuric ions.[10] More recently, iron oxide nanoparticles coated with humic acid showed remarkable capability to remove heavy metal ions (Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}) from water.[11] Metal chalcogenides with ion exchange properties represent a new class of materials with very promising remediation properties for heavy metal ions.[12,13] A great advantage of metal chalcogenides over functionalized sorbents is that they display innate selectivity for soft metal ions[12–14] because of the ability to form M–S bonds and therefore, there is no need for incorporation of functional groups into their frameworks. The huge potential of sulfide-based ion exchangers as heavy metal ion sorbents was particularly demonstrated by the layered material K$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$ (x $=$ 0.5–0.95) (KMS-1).[13]

Herein, we report the solid acid H$_{2x}$Mn$_x$Sn$_{3-x}$S$_6$ [(x $=$ 0.11–0.25)] or LHMS-1 (for Layered Hydrogen Metal Sulfide-1) that is exceptionally stable in acids. LHMS-1 is a rare example of a solid acid in the class of sulphides. Its affinity and selectivity for Hg^{2+} exceeds those of its precursor KMS-1. LHMS-1 was found highly effective for mercury capture over a very broad pH range. Remarkably, its high affinity and selectivity for Hg^{2+} persists even under extremely acidic conditions (for example, in the presence of highly concentrated $\sim$6 M HCl or HNO$_3$ acids). This property of LHMS-1, in combination with its very high acid stability, makes it a superior sorbent for the efficient removal of Hg^{2+} from highly acidic waste. Hg^{2+}-laden samples showed an exceptional capability to retain their mercury under various conditions indicating their possible suitability as final waste form. The pristine material, however, can be regenerated and reused without loss of its initial exchange capacity.
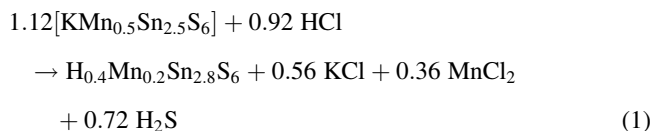
2. Results and Discussion

2.1. Synthesis and Characterization

LHMS-1 material has a plate-like morphology (Fig. 1) and is formed by the acid-induced transformation of KMS-1. The chemical equation for the conversion of e.g. KMn$_{0.5}$Sn$_{2.5}$S$_6$ to

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Figure 1. a) LHMS-1 material formed as plate-like grey specimens; b) Scanning Electron Microscopy (SEM) image of the same material.

$H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ can be written as follows:

$$1.12[KMn_{0.5}Sn_{2.5}S_6] + 0.92\ HCl$$
$$\rightarrow H_{0.4}Mn_{0.2}Sn_{2.8}S_6 + 0.56\ KCl + 0.36\ MnCl_2$$
$$+ 0.72\ H_2S \qquad (1)$$

According to this equation, LHMS-1 is formed by the transformation of KMS-1 which involves the partial removal of manganese from the layers and attachment of H^+ to sulfide atoms in the structure. This step also involves some release of H_2S which was proven by the precipitation of black HgS upon addition of $Hg(NO_3)_2$ to the filtrate solution after the acid treatment.

Powder X-ray Diffraction (PXRD) measurements showed that LHMS-1 (Fig. 2a) is a layered material and isostructural to SnS_2.[15] The Sn, Mn and S content of LHMS-1 was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Energy Dispersive Spectroscopy (EDS) analyses. IR spectroscopy confirmed the formation of S–H bonds by the appearance of a new band at 2403 cm^{-1} (Fig. 2c).[16] The existence of protons in LHMS-1 was also probed with pyrolysis mass spectroscopy that showed the release of H_2S upon heating the material at $\sim440\,^{\circ}$C [as shown by eq(S1), Supporting Information]. The proton content of LHMS-1 was determined with Thermogravimetric Analyses (TGA) based on the quantity of H_2S released from LHMS-1 by heating it (see supporting information). The TGA also indicated existence of ~1–1.25 H_2O per formula unit of LHMS-1.

Density measurements performed on LHMS-1 (see supporting information) indicate a density of $3.65\,g\,cm^{-3}$ which is significantly lower than the $4.69\,g\,cm^{-3}$ calculated based on PXRD indexing data. Therefore, the density measurements revealed that the transformation of KMS-1 to LHMS-1 leads to a structure which may contain vacancies created by the removal of Mn^{2+} ions.

$H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ displays a band gap energy of ~1.0 eV, which is ~1.5 eV lower than that of SnS_2 (Fig. 2c). The band gap of LHMS-1 is also lower than that (~1.3 eV) of $K_{2x}Mn_xSn_{3-x}S_6$ (x = 0.5–0.95) (KMS-1).[13] This large difference in the band gaps of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ and SnS_2 may be attributed to the substitution of ($\sim7\%$) Mn for Sn in the first material. In addition, the band gap of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ is influenced by interactions of the protons with the layer S atoms. The effective magnetic moment for LHMS-1 was found 5.6 B.M. per manganese ion which is in good agreement with the theoretical magnetic moment for Mn^{2+} (5.9 B.M.) (see Supporting Information).

The H^+ ions in LHMS-1 are mobile and exchangeable and in combination with the basic sulfide ligands of the layers give rise to facile ion exchange with Hg^{2+} and Ag^+ in aqueous solutions. Analytical data [EDS and Inductively Coupled Plasma-Mass Spectroscopy(ICP-MS)] revealed the presence of ~0.2 mol of Hg^{2+} and ~0.7 mol[17] of Ag^+ per formula unit of the corresponding exchanged products. PXRD (Fig. 2a,b) patterns of Hg^{2+}-exchanged compounds were almost identical to those of the pristine samples [only a small shift ($\sim0.2\,^{\circ}$) of the (001) reflection to higher 2θ angles (Fig. 2a,b) was observed for some Hg^{2+}-exchanged products].[15] In fact, the d_{001} (~5.82 Å) of Hg^{2+}-exchanged LHMS-1 is very close to the d_{003} (~5.81 Å) of the Hg^{2+}-exchanged analogue of KMS-1[13] which indicates an interlayer space of ~5.8 Å is suitable for the accommodation of Hg^{2+}. The Ag^+-exchanged compound displayed a longer interlayer space (6.10–6.17 Å) than that of pristine LHMS-1 and its Hg^{2+}-exchanged analogue (Fig. 2a,b).[15]
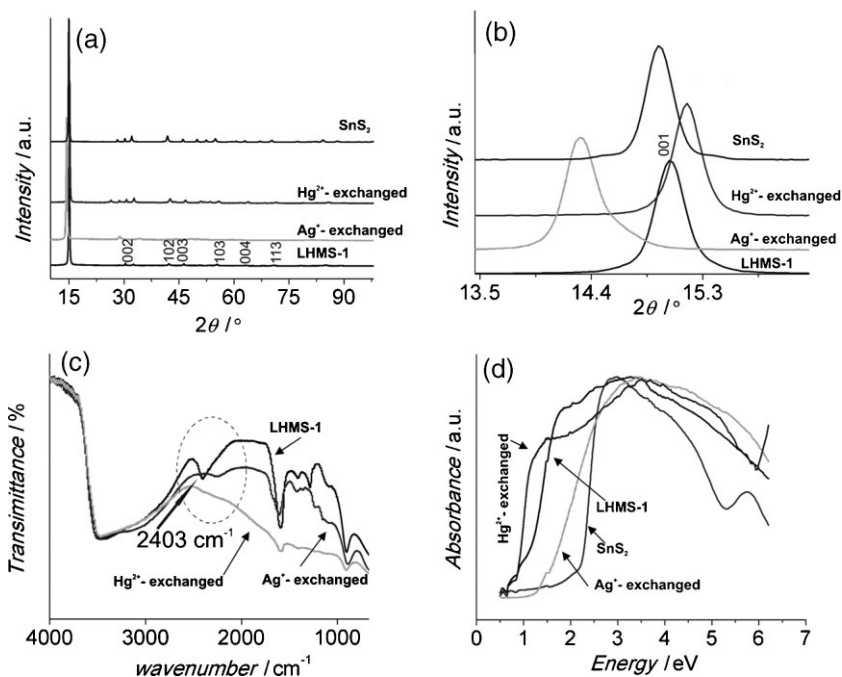

Figure 2. a) PXRD patterns for pristine LHMS-1 (with the indexing of selected peaks), SnS_2 and Hg^{2+}, Ag^+-exchanged material; b) Enlarged view of the (001) peaks of these patterns; c) Mid-IR spectra of pristine LHMS-1a and Ag^+ and Hg^{2+}-exchanged materials. The H-S peak at 2403 cm^{-1} present in the spectrum of LHMS-1a disappeared in the spectra of Ag^+ and Hg^{2+}-exchanged materials. This is highlighted by drawing a circle; d) Solid state NIR-UV-Vis spectra for pristine LHMS-1, SnS_2, Hg^{2+} and Ag^+-exchanged materials.

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2.2. Spectroscopy and Local Structure

The replacement of protons of compound LHMS-1 after the Hg^{2+} and Ag^+ ion-exchange processes is supported by Infrared spectroscopy. Specifically, the characteristic IR peak of H-S bonds of LHMS-1 at 2403 cm^{-1} was absent in the IR spectra of the Ag^+- and Hg^{2+}-exchanged materials, revealing the complete removal of H^+ (Fig. 2b). In addition, the insertion of Hg^{2+} and Ag^+ was further probed by solid-state NIR-UV-Vis reflectance data. The Hg^{2+}-exchanged compound exhibits a considerably lower band gap ($\sim$0.8 eV) than that of LHMS-1 (Fig. 2c). This is consistent with the fact that the Hg–S covalent interactions are stronger than the H–S ones. A blue shift of $\sim$0.4 eV is observed for the Ag^+-exchanged material (Fig. 2c). This can be explained by taking into account that the intercalation of Ag^+ ions resulted in a significant expansion (0.3–0.4 Å) of the interlayer space of LHMS-1 and therefore, in weaker interlayer interactions.

To probe the local structure of the Hg atoms in the interlayer space of LHMS-1 we performed synchrotron radiation diffraction and atomic PDF (Pair Distribution Function) studies on LHMS-1 and Hg-loaded LHMS-1 samples. The experimental PDF for these materials is shown in Figure 3a. The data for LHMS-1 may be fit very well with a structure model based on SnS_2 structure (space group $P6_3mc$) with parameters a = 3.624 Å, c = 12.09 Å, Sn at (2/3,1/3,1/8) with atomic displacement parameters $\beta_{11} = \beta_{22} = 0.0055$ Å^2 and $\beta_{33} = 0.312$ Å^2, S1 at (0,0,0) and S2 at (1/3,2/3,1/4) both with $\beta_{11} = \beta_{22} = \beta_{33} = 0.0045$ Å^2 The increased β_{33} of Sn atoms reflects the presence of a considerable turbostratic disorder between the layers of (Metal = Sn/Mn)-S_6 units in LHMS-1. The experimental PDF for Hg^{2+}-LHMS may be also described very well with a structure model based on the SnS_2–type structures (space group $P6_3mc$) with parameters a = 3.602 Å, c = 12.20 Å, Sn atoms at (2/3,1/3,1/8) with $\beta_{11} = \beta_{22} = 0.004$ Å and $\beta_{33} = 0.075$ Å^2, S1 at (0,0,0) and S2 at (1/3,2/3,1/4) both with $\beta_{11} = \beta_{22} = \beta_{33} = 0.004$ Å^2; and Hg at (2/3,1/3,3/8) $\beta_{11} = \beta_{22} = 0.05$ Å^2, and $\beta_{33} = 0.10$ Å^2. Interestingly according to the PDF analyses the interlayer disorder in LHMS-1 diminishes with the intercalation of Hg^{2+} (i.e. β_{33} for the metal atoms drops from about 0.3 Å^2 to about 0.075 Å^2). This is due to the replacement of protons in LHMS-1 by Hg^{2+} ions that obviously serve as "bridges" between the layers Sn/Mn-S_6 units to reduce the turbostratic disorder. According to the PDF model, the coordination of Hg^{2+} with the layer sulfide atoms is
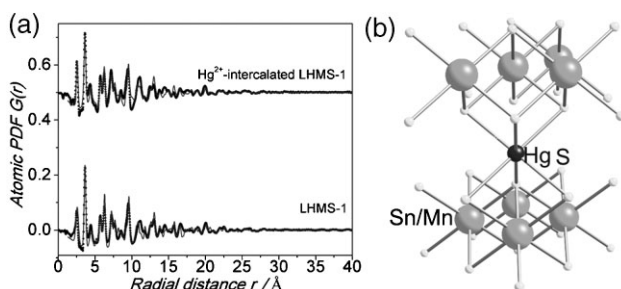
Figure 3. a) Experimental (symbols in black) atomic PDFs for LHMS-1 and LHMS-1 intercalated with Hg^{2+}. Atomic PDFs computed (solid line) on the basis of SnS_2–type structure models are given as well; b) The octahedral coordination of Hg^{2+} in the structure of Hg^{2+}-laden LHMS-1, which is indicated by the PDF model.

octahedral (Fig. 3b) with Hg–S bond distances of $\sim$2.57 Å. Octahedral coordination for mercury, although not very common, is known in the structures of some mercury-containing sulfide materials.[18]

2.3. Mercury Capture and Remediation

To evaluate the capability of LHMS-1 as Hg^{2+} scavenger and its potential for environmental remediation, Hg^{2+} ion-exchange equilibrium and kinetic studies as well as exploration of the acidity/basicity of the solutions on the mercury absorption were performed. The Hg^{2+} content of the solutions before and after the ion-exchange reactions was analyzed with ICP-MS.

The Hg^{2+} uptake from solutions of various concentrations was studied for LHMS-1 ($H_{0.5}Mn_{0.25}Sn_{2.75}S_6 \cdot H_2O$) with the batch method ($V{:}m = 1000$ mL/g, pH$\sim$5, contact time $\sim$12 h, room temperature).[19] The release of H^+ ions from LHMS-1 to the solutions was reflected in the reduction of their pH values. For example, the pH of a solution initially containing $\sim$70 ppm Hg^{2+} decreased from $\sim$5 to $\sim$3.5, after ion-exchange with LHMS-1.

The mercury ion-exchange equilibrium data are presented in Figure 4a. The fit of the data was achieved with the Langmuir–Freundlich (LF) isotherm model (correlation coefficient $R^2 = 0.966$) expressed as

$$q = qm \frac{(bCe)^{\frac{1}{n}}}{1 + (bCe)^{\frac{1}{n}}} \qquad (2)$$

where q (mg/g) is the amount of the cation absorbed at the equilibrium concentration C_e (ppm), q_m is the maximum absorption capacity of the sorbent, b and n are constants.[20]

This model predicts a maximum Hg^{2+} exchange capacity of compound LHMS-1 equal to 87 ± 6 mg g^{-1} which is in good agreement with the theoretical capacity (91 mg g^{-1}) calculated by the formula $H_{0.5}Mn_{0.25}Sn_{2.75}S_6 \cdot H_2O$. The tremendous affinity of LHMS-1 for Hg^{2+} is reflected in the calculated (from the equilibrium exchange data) distribution coefficient K_d^{Hg} values ranging from 1.49×10^6 to 6.41×10^6 mL g^{-1}. These K_d values for LHMS-1 exceed those reported for commercial resins (10^4–5.10×10^5 mL g^{-1})[8c,21] and silane chelating fibers (3.00×10^5–3.80×10^6 mL g^{-1})[22]. In addition, they are well comparable with the K_d^{Hg} values for chalcogel-1 (9.5×10^6–1.6×10^7)[14] and for mesoporous thiol-functionalized silicates (3.40×10^5–1.01×10^8 mL g^{-1}).[8] Note also that the K_d^{Hg} values for LHMS-1 are higher than those for KMS-1 [3.50×10^4–3.90×10^5 mL g^{-1}],[13] indicating a higher affinity of LHMS-1 for Hg^{2+}.

Ion exchange reactions of LHMS-1 with Hg^{2+} solutions (0.8–1 ppm) at various pH values (0–9) were performed. The results (Table 1) showed that the percentage of mercury removal remained very high (97.9–99.9%) in the entire tested pH range. The capability of LHMS-1 to absorb Hg^{2+} under extremely acidic conditions is remarkable. For example, LHMS-1 could quantitatively ($\geq$99.9%) remove mercuric ions in presence of HCl 3.6 M or HNO$_3$ 6 M (Table 1). The K_d^{Hg} values (Table 1) found for the experiments with the highly concentrated acidic solutions were some of the highest ever reported (4×10^6–10^7 mL g^{-1}). Note that
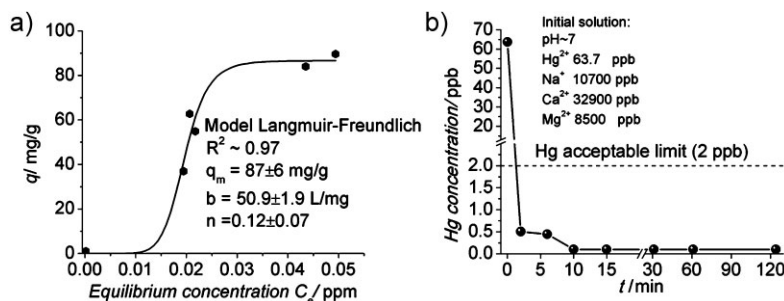
Figure 4. a) Equilibrium data for mercury absorption by LHMS-1 [q (mg g^{-1}) is the amount of Hg^{2+} absorbed at the equilibrium concentration C_e (ppm)]. The black line represents the fitting of the data with the Langmuir-Freundlich model; b) Kinetics for the decontamination of potable water from Hg^{2+} using LHMS-1.

mesoporous carbon with functional thio-pyrene groups and sulfur-impregnated activated carbon shows much lower K_d^{Hg} values ($5-7 \times 10^5$ mL g^{-1}) even under less acidic conditions (pH~1).[10] In addition, Li$_{1.3}$MoS$_2$ exhibits very high K_d^{Hg} values ($>10^6$ mL g^{-1}) in the presence of 0.1 M HNO$_3$ acid.[23] However, Li$_{1.3}$MoS$_2$ is air sensitive and deactivates quickly.[23]

Therefore, LHMS-1 may be useful for mercury remediation of extremely acidic waste water, e.g. such as present in nuclear waste facilities.[7a] We should note that the only other example of a material highly effective for mercury capture under extremely acidic conditions (pH $\leq$ 0) is a thiol-functionalized organoceramic composite.[7a] Such thiol-functionalized sorbents, however, are not suitable for long-term use because the thiol groups have a great tendency to oxidize to disulfide ones under ambient conditions (e.g. they need to be stored under inert conditions[7c]), causing a gradual loss of the capacity of these sorbents.[7b] In contrast, LHMS-1 is extremely stable in air and water (from pH less than zero to 12) because its structure is based on a robust SnS$_2$- type layer and does not lose its capacity for mercuric ions.[13]

Competitive experiments with the simultaneous presence of Hg^{2+} (0.035 mM), Ag$^+$ (0.098 mM), Pb^{2+} (0.040 mM) and Cd^{2+} (0.087 mM) were also conducted. The ratio of the total moles of the metal ions to the moles of LHMS-1 material was ~0.04, i.e. the material could quantitatively absorb all ions without saturating its exchange sites. The ICP-MS analysis data for the solutions after the ion-exchange processes revealed that Hg^{2+} and Ag^{2+} were quantitatively absorbed (99.99%), while less (87–88%) of the

initial Pb^{2+} and Cd^{2+} amounts were removed from the solution (Table 1). The higher preference of LHMS-1 for sorption of Hg^{2+} and Ag$^+$ over Pb^{2+} and Cd^{2+} is particularly pronounced in the K_d^{Hg} and K_d^{Ag} values being 10^3-10^4 times higher than the distribution coefficient values for Pb^{2+} and Cd^{2+}. This result is consistent with the fact that LHMS-1 is selective for cations with higher softness (i.e. Hg^{2+}, Ag$^+$ vs. Pb^{2+}, Cd^{2+}) which are able to substitute the interlayer protons of this material.

In order to evaluate the ability of LHMS-1 to absorb Hg^{2+} ions under realistic conditions, we tested it with potable water (pH~7, $V{:}m \sim 1000$ mL g^{-1}) intentionally contaminated with environmentally relevant (highly toxic) levels of mercury (67 ppb). Note that background electrolytes were in huge excess in relation to mercuric ions (e.g. the concentration of calcium was ~2590 times higher than that of Hg^{2+}). To enhance the rate of the mercury absorption, the material was pre-treated with sonication for 1–1:30 h.[13] Remarkably, LHMS-1 was able to reduce the concentration of Hg^{2+} well below the acceptable limits in drinking water (2 ppb)[24] within only 2 min of LHMS-1/water contact (Fig. 4b). This result indicated the potential of using LHMS-1 as a highly effective filter for immediate decontamination of water from Hg^{2+} ions.

Hydrothermal leaching tests of Hg^{2+}-exchanged products of LHMS-1 performed at 70 °C for one week showed Hg^{2+} release of ~1.3% of its total amount to the solution as well as negligible leaching of Sn (0.3%), Mn (0%) and S (2.9%). Note that the hydrothermal treatment of Hg-laden mesoporous thiol-functionalized silicates (SAMMS) at 70 °C for only one day resulted in removal of ~3.6% of their total Hg content, from which 2.9% and 0.7% was surface-bound and covalently bound Hg respectively.[8c] Thus, the binding of mercury in Hg^{2+}-exchanged LHMS-1 seems to be as strong as or even stronger than that of mercury in Hg-laden SAMMS. In addition, the high hydrolytic stability and exceptional Hg binding capacity of Hg-laden LHMS-1 suggest that this material may be considered as a permanent waste form without need for a secondary treatment. However, further tests are likely necessary prior to approval of a waste material for land disposal.[8c]

Table 1. Selected data for Hg^{2+} ion exchange of LHMS-1. The $V{:}m$ ratio used in these experiments was ~1000 mL g^{-1} with the exception of Hg^{2+}-Pb^{2+}-Cd^{2+}-Ag$^+$[a] experiment performed with $V{:}m$ ratio of 294 mL g^{-1}.

Metal ion	Initial concentration (ppb)	Final concentration (ppb)	% Removal	K_d (mL g^{-1})
Hg^{2+}/(pH ~ 0)	983	0.1	99.99	9.83×10^6
Hg^{2+}/(pH ~ 3)	959	0.3	99.96	3.20×10^6
Hg^{2+}/(pH ~ 6)	996	0.2	99.98	6.41×10^6
Hg^{2+}/(pH ~ 9)	802	17	97.88	4.62×10^4
Hg^{2+}/HCl (3.6 M)	1085	0.1	99.99	1.09×10^7
Hg^{2+}/HNO$_3$ (6.0 M)	14180	333	99.99	4.09×10^6
Hg^{2+}	6990	0.3	99.99	6.85×10^6
Pb^{2+}	8185	1058	87.07	1.98×10^3
Cd^{2+}	9780	1118	88.57	2.28×10^3
Ag$^+$	10585	0.2	99.99	1.56×10^7

[a] pH of the initial solution ~1. 5.

The strongly bound Hg^{2+} cannot be leached out from Hg-laden LHMS-1 even with 6 M HCl solutions. Much higher HCl concentrations, however, ~ 12 M can accomplish the complete removal of Hg^{2+} from Hg-loaded LHMS-1 and the regeneration of the original material. Compounds $H_{2x}Mn_xSn_{3-x}S_6$ with $x = 0.2$–0.25 display high solubility in HCl 12 M. In contrast, analogues with lower amount of manganese [i.e. $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.11$–0.15)] showed much less solubility in 12 M HCl solutions. Therefore, regeneration of $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.11$–0.15) was possible by reacting Hg-laden samples with 12 M HCl acid. This process resulted in ~ 93–98% removal of Hg^{2+} from the solid as found by ICP-AES or MS. The regenerated material displayed identical XRD pattern as the pristine material. The regeneration procedure, however, caused the dissolution of ~ 40–60% of the material. The usability of the regenerated LHMS-1 product was demonstrated by ion-exchange of a sample (10 mg) with Hg^{2+} (54 ppm, 0.15 equiv.) solution (10 mL) yielding a final Hg^{2+} concentration of 13 ppb (99.98% removal).

3. Conclusions

The novel stable sulfide acid $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.11$–0.25) [LHMS-1] can be prepared by acid-induced rearrangement of $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5$–0.95). This new material displayed exceptional selectivity for the softer metal ions like Hg^{2+} and Ag^+ and against cations of lower softness such as Pb^{2+} and Cd^{2+}. The affinity and binding capacity of LHMS-1 for Hg^{2+} were found enormous and reach those of the most efficient mercury adsorbents. LHMS-1 has a unique characteristic, which distinguishes it from other mercury sorbents: To our best knowledge it represents the only highly stable material in air and water with excellent efficiency for remediation of mercury in extremely acidic environment (pH < 0). Therefore, this sorbent may find practical applications for efficient treatment of wastes, in cases where existing materials cannot function. The Hg-laden samples of LHMS-1 material may be considered as final waste forms, avoiding the step of secondary waste treatment, because of their excellent hydrolytic stability and capability to retain their mercury content even under harsh acidic conditions (in the presence of HCl ≤ 6 M).

4. Experimental

Synthesis of $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.2$–0.25): Compound $K_{1.9}Mn_{0.95}Sn_{2.05}S_6 \cdot 2H_2O$ (0.35 mmol, 0.209 g)[25] was added as a solid in 20 mL HCl (0.6 M) solution. The mixture was kept under magnetic stirring for ≈ 12 h. This procedure was performed twice in order to ensure complete conversion of $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$ to the proton-containing material. Then, the grey solid was isolated by filtration, washed several times with water, acetone and ether and dried in the air (Yield based on $K_{1.9}Mn_{0.95}Sn_{2.05}S_6 \cdot 2H_2O$: 0.115 g, 80.3%). EDS analysis on various samples prepared gave the average formula "$Mn_{0.3}Sn_{2.7}S_{5.6}$". Accurate determination of the Sn and Mn content of various samples by ICP-AES is consistent with the formula $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.2$–0.25) [proton content was determined based on thermal analysis results (see supporting information) and sulfur content was calculated based on charge balance considerations].

Synthesis of $H_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.11$–0.15): Materials with such compositions were prepared with a similar procedure as $H_{2x}Mn_xSn_{3-x}S_6$

($x = 0.2$–0.25) with the difference that the pristine $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$ used was prepared with hydrothermal synthesis (the pristine $K_{1.9}Mn_{0.95}Sn_{2.05}S_6$ used for the preparation of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$, was prepared with solid state synthesis). Pristine materials prepared with hydrothermal synthesis are usually finer powders than those prepared with solid state synthesis. Therefore, more Mn is leached out during the acid treatment of KMS-1 hydrothermally synthesized likely due to its finer powder form.

Ion-Exchange Experiments: A typical ion-exchange experiment of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ with Hg^{2+} is the following: In a solution of $HgCl_2$ (0.037 mmol, 10.0 mg) in water (20 mL), compound $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ (0.185 mmol, 103.0 mg) was added as a solid. The mixture was kept under magnetic stirring for ≈ 12 h. Then, the polycrystalline material was isolated by filtration, washed several times with water, acetone and ether and dried in the air. No difference in the Hg^{2+} exchange capacity of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ was observed when the nitrate salt of this metal ion was used in the ion exchange experiments instead of its chloride analogue. In most cases, the Hg^{2+} exchange was completed after one cycle.

A similar experimental route was followed for the ion-exchange of $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ with Ag^+ except that 0.4 equivalents of $AgNO_3$ (with respect to the pristine material) were used. The vial, where the Ag^+-exchange reaction was performed, was wrapped with aluminium foil in order to avoid light-induced reduction of Ag^+ to metallic silver. Two cycles of ion exchange were needed for isolation of the fully Ag^+-exchanged product.

The Hg^{2+} uptake from solutions of various concentrations was studied by the batch method at $V:m \sim 1000$ mL/g, room temperature and 12 h contact. These data were used for the determination of Hg^{2+} sorption isotherm. The competitive and variable pH ion exchange experiments of LHMS-1 were also carried out with the batch method at $V: m$ ratio (294–1000) mL g^{-1}, room temperature and 12 h contact (only reactions with alkaline solutions were performed for 1–2 h to prevent the exfoliation of LHMS-1 occurring with longer reaction times under such conditions). Reactions with highly concentrated hydrochloric solutions were conducted for 12 h. The reactions with HNO_3 solutions were performed for 30 min–2 h to avoid oxidation of LHMS-1.

The distribution coefficient K_d, used for the determination of the affinity and selectivity of LHMS-1 for Hg^{2+}, Cd^{2+}, Pb^{2+} and Ag^+, is given by the equation

$$K_d = \frac{V[(C_0 - C_f)/C_f]}{m} \tag{3}$$

where C_0 and C_f are the initial and equilibrium concentration of M^{n+} (ppm), V is the volume (mL) of the testing solution and m is the amount of the ion exchanger (g) used in the experiment [20].

Kinetic Studies: Hg^{2+} ion-exchange experiments of various reaction times (2, 5, 15, 30, 60, 120 min) have been performed. For each experiment, a total of 10 mg of LHMS-1 was weighted into a 20 mL glass vial. A 10 mL sample of potable water intentionally contaminated with Hg^{2+} (63.7 ppb) was added to each vial and the mixtures were kept under magnetic stirring for the designated reaction times. The suspensions from the various reactions were filtrated and the resulting solutions were analyzed for their mercury content with ICP-MS.

Hydrothermal Stability Leaching Studies of Hg-Laden Samples: Samples of ~ 5–10 mg of Hg-laden $H_{0.4}Mn_{0.2}Sn_{2.8}S_6$ were placed in ~ 10 mL deionized water in 20 mL vials. The vials were tightly capped and kept in a sand bath at 70 °C for one week. Then, the solutions were filtered and analyzed for their mercury, tin, manganese and sulfur content with ICP-AES.

Regeneration: Samples of ~ 34 mg of Hg-laden compounds were treated for ~ 12 h with ~ 10 mL solutions containing 12 M HCl. After this treatment, the samples were analyzed for their Hg content with ICP-AES or MS.

Experimental details for the various physical and analytical measurements (ICP-MS, ICP-AES, density measurements, pyrolysis-MS, PDF, variable temperature magnetic susceptibility measurements, IR, EDS, solid-state UV-Vis, TGA analyses), TGA graphs and magnetic susceptibility data are given in the Supporting Information section.

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