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Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams Using Redox-active Layered Metal Chalcogenides

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Research Objective

Mercury and other highly-toxic heavy metals such as cadmium and lead are present in many aquatic environments, and the remediation of such environments or the avoidance of heavy-metal contamination in the first place is an area of active interest. In recent years tougher environmental regulations and the high initial cost of new, more effective, and more selective extractants has made the reuse of extractant materials and the minimization of secondary waste volume a focus of our scientific effort. Our research has involved the investigation of redox-active layered metal chalcogenides as selective, effective, and redox-recyclable extractants for heavy metals from aqueous solution.

Research Progress and Implications

The use of lithium-intercalated transition-metal dichalcogenides, Li_xMS_2 , as redox-recyclable ion-exchange materials for the extraction of the aqueous heavy-metal ions Hg^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} was investigated ($0.25 = x = 1.9$; $\text{M} = \text{Mo}, \text{W}, \text{Ti}, \text{Ta}$). For Li_xTiS_2 and Li_xTaS_2 , hydrolysis produced $\text{S}^{2-}(\text{aq})$ ions which precipitated $\text{Hg}(\text{II})$ as $\text{HgS}(\text{s})$. In contrast, the materials Li_xMoS_2 and Li_xWS_2 did not undergo hydrolysis to form S^{2-} ions. Instead, ion-exchanged materials such as $\text{Hg}_{0.50}\text{MoS}_2$ and $\text{Pb}_{0.15}\text{MoS}_2$ were isolated. The selectivity of Li_xMoS_2 for the heavy-metal ions was $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The affinities for the latter three ions, but not for Hg^{2+} , increased when the extractions were performed under anaerobic conditions. When Hg_yMoS_2 was heated under vacuum at 425°C , an entropy-driven internal redox reaction resulted in deactivation of the extractant, producing essentially mercury-free MoS_2 and a near-quantitative amount of mercury vapor (collected in a cold trap). The ratio of the volume of metallic mercury (secondary waste) to the volume of $10.0 \text{ mM Hg}^{2+}(\text{aq})$ (primary waste) was 1.5×10^{-4} . Samples of MoS_2 produced by heating Hg_yMoS_2 were reactivated to Li_xMoS_2 by treatment with *n*-butyllithium. Some samples were used for three cycles of extraction, deactivation/recovery, and reactivation with a primary waste simulant consisting of $10 \text{ mM Hg}^{2+}(\text{aq})$ in 0.1 M HNO_3 with no loss in ion-exchange capacity. When the Mo/Hg molar ratio was 5.0 and the initial $[\text{Hg}^{2+}(\text{aq})] = 1 \text{ mM}$, only $0.033(2) \text{ }\mu\text{M}$ mercury (6.5 ppb) was detected in the filtrate after the extraction step. The highest observed capacity of Li_xMoS_2 for $\text{Hg}^{2+}(\text{aq})$ was $580 \text{ mg mercury per g Li}_{1.9}\text{MoS}_2$. Initial experiments have indicated that Li_xWS_2 is also a redox-recyclable extractant for $\text{Hg}^{2+}(\text{aq})$.

Since two of the lithium-intercalated transition metal dichalcogenides, Li_xMoS_2 and Li_xWS_2 , investigated showed promise as effective, selective, and redox-recyclable extractants for heavy metal ions from aqueous solution we decided to study of the mechanisms of activation, extraction, deactivation, and recovery of the extractant and the target ion. This investigation has involved the use of powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and X-ray absorption spectroscopy (XAS). Based on our results, we believe that heavy-metal ions are removed from solution by a reversible ion-exchange process with the negatively charged metal chalcogenide layers. The extracted heavy-metal ions are present in the interlayer space of the layered solid-state extractant. We have also determined that the metal ions are present, in the heavy-metal-loaded extractant, in a sulfur rich coordination environment and that the heavy-metal ions are in an oxidized form. The

XAS investigation indicated that the selectivity of the extractants may be based on the ability of certain heavy-metal ions to stabilize the negatively charged (reduced) metal-chalcogenide layers (that have a distorted geometry relative to the neutral (oxidized) metal-chalcogenide layer). The stabilization ability of the metal ions appears to correlate strongly with their degree of soft-Lewis acid character. The softer Lewis acids, such as Hg^{2+} and Ag^+ , are very effective at stabilizing the reduced chalcogen layers and are hence removed to a large extent. However, metal ions such as Ni^{2+} , Zn^{2+} , and Mn^{2+} , that are harder Lewis acids than Hg^{2+} and Ag^+ , are not as effective at stabilizing the reduced chalcogen layers and hence are removed to a far lesser extent than both Hg^{2+} and Ag^+ .

Planned Activities

We are actively investigating both the optimization of the Li_xMoS_2 and Li_xWS_2 extractants and the development of new redox-active layered extractants. Both the Li_xMoS_2 and Li_xWS_2 extractants do generate some hydrogen gas during the extraction process. Naturally, we would like to eliminate this potentially dangerous side product and are currently synthesizing Li_xMoS_2 and Li_xWS_2 extractants that will generate no hydrogen and are still effective extractants. We have shown that Li_xMoS_2 is an effective, selective, and redox-recyclable extractant for $\text{Hg}^{2+}(\text{aq})$ through at least three complete cycles of activation/extraction and reactivation/recovery. We would like to study both of the Li_xMoS_2 and Li_xWS_2 extractants through many more cycles of activation/extraction and reactivation/recovery. We are also interested in studying the feasibility of using electroactive conducting polymer films containing MoS_2 and WS_2 particles for effective, selective, and redox-recyclable extraction of heavy-metal ions from aqueous solution.

There are new alkali-metal-intercalated metal chalcogenides that remain to be investigated. Three such materials that will be studied are the lithium-intercalated SnS_2 , VS_2 , and NiPS_3 compounds. All of these materials have been synthesized previously as Li_xMS_2 or Li_xMPS_3 and will be tested by the methods we have developed for our Li_xMS_2 ($\text{M} = \text{Mo}, \text{W}, \text{Ti}, \text{Ta}$) studies.

Other Access To Information

Gash, A.E.; Spain, A.L.; Dysleski, L.M.; Flaschenriem, C.J.; Kalaveshi, A.; Dorhout, P.K.; Strauss, S.H. *Environ. Sci. Technol.* 1998, 32, 999.

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