J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article
pubs.acs.org/JACS

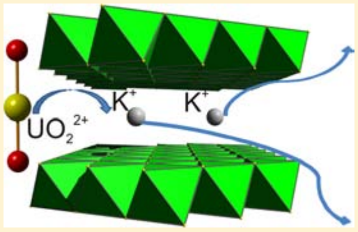
Layered Metal Sulfides Capture Uranium from Seawater

Manolis. J. Manos and Mercouri G. Kanatzidis*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

Supporting Information

ABSTRACT: Uranium is the main source for nuclear energy but also one of the most toxic heavy metals. The current methods for uranium removal from water present limitations, such as narrow pH operating range, limited tolerance to high salt concentrations, or/and high cost. We show here that a layered sulfide ion exchanger $K_2MnSn_2S_6$ (KMS-1) overcomes these limitations and is exceptionally capable in selectively and rapidly sequestering high (ppm) as well as trace (ppb) quantities of UO_2^{2+} under a variety of conditions, including seawater. KMS-1 can efficiently absorb the naturally occurring U traces in seawater samples. The results presented here reveal the exceptional potential of sulfide-based ion-exchangers for remediating of uranium-containing wastes and groundwater and for extracting uranium from the sea.



INTRODUCTION

The current increased interest in nuclear power as a potential and sustainable solution to the energy problem raises serious concerns about the hazardous impact of radioactive and toxic waste on the environment, natural water resources, and the human health. The major source for nuclear energy is uranium salts,[1] which are released to the environment from nuclear fuel fabrication, ore mining, manufacturing, and processing. A large legacy of uranium-contaminated sites was also left behind with the closure of many facilities producing nuclear and chemical weapons worldwide.

A variety of technologies and materials have been evaluated as means of attenuating uranium concentrations, which exists primarily as uranyl cation UO_2^{2+} (free or complexed with hydroxyl or carbonate ligands) in aqueous solutions under oxic conditions.[1] Examples of such methods comprise ion-exchange/absorption,[2−4] adsorption,[5−7] and chemical/biochemical reductive precipitation.[8−11] Adsorption and reductive precipitation, however, are governed by surface-occurring processes easily inhibited by oxidation, contamination, and clogging.[12] In contrast, the sorption of ions by ion-exchangers is a bulk property of the materials, and therefore, it is not amenable to the phenomena, limiting the performance of the surface-based technologies. Inorganic ion-exchangers such as clays and zeolites are generally of higher chemical, thermal, and radiolytic stability as well as more affordable compared to the organic resins. However, the inorganic exchangers absorb heavy metals (e.g., uranyl ion UO_2^{2+}) only within a very narrow pH (4−7) range (due to their "poisoning" by proton ions and instability in pH extremes) and in the presence of relatively low salt concentrations.[13,14] Furthermore, the slow exchange kinetics of large hydrated cations (e.g., $[Sr(H_2O)_x]^{2+}$, $[UO_2(H_2O)_x]^{2+}$, etc.) shown by zeolites limits their applicability for effective treatment of solutions contaminated with such cations.[15]

In general, uranyl is considered a hard cation in the Lewis acid sense, considering the hexavalent oxidation state of the uranium.[16] However, compounds with uranyl cations forming strong covalent bonds with soft S^{2-} groups have been reported.[17] To our knowledge, the only sorbents with exclusively soft ligands tested as uranyl scavengers are mineral sulfides (such as FeS_2). These materials can remove some UO_2^{2+} through reduction of the uranium(VI) and precipitation of the insoluble U_3O_8 and are effective only when their surfaces are freshly polished.[12,18,19]

Herein we report the UO_2^{2+}-exchange properties of the layered sulfide $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5−0.95$), KMS-1, which was previously shown to be a very efficient sorbent for Sr^{2+} and Cs^+ cations as well as an extraordinarily effective soft heavy metal ion (Hg^{2+}, Pb^{2+}, Cd^{2+}) scavenger.[20−22] Through detailed studies, we show that KMS-1 displays an extraordinary affinity and selectivity for UO_2^{2+}, which makes it one of the most powerful U sorbents ever reported. In addition, the high potential of KMS-1 is demonstrated by its excellent performance as U scavenger with real world water samples (e.g., potable and lake water) and its highly effective absorbtion of the naturally occurring U in seawater, with total estimated reserves of U 1000 times more than those of the terrestrial ores.

EXPERIMENTAL SECTION

Materials. The preparation of compound KMS-1 is reported in ref 20.

UO_2^{2+} Ion-Exchange Experiments with KMS-1. A typical ion-exchange experiment of KMS-1 with UO_2^{2+} is the following: To a solution of $UO_2(NO_3)_2 \cdot 5H_2O$ (0.02 mmol, 10 mg) in water (10 mL) was added compound KMS-1 (0.018 mmol, 10 mg) as a solid. The mixture was kept under magnetic stirring for ≈12 h. Then, the polycrystalline material, which had a much darker color compared to the pristine KMS-1 material, was isolated by centrifugation, washed several times with water and acetone, and dried in the air. Energy Dispersive Spectroscopy (EDS) analysis on the material gave the average formula "$U_{0.8}Mn_{0.9}Sn_{2.3}S_6$". The U:Mn:Sn molar ratio

Received: August 12, 2012
Published: September 25, 2012

dx.doi.org/10.1021/ja308028n | *J. Am. Chem. Soc.* 2012, 134, 16441−16446

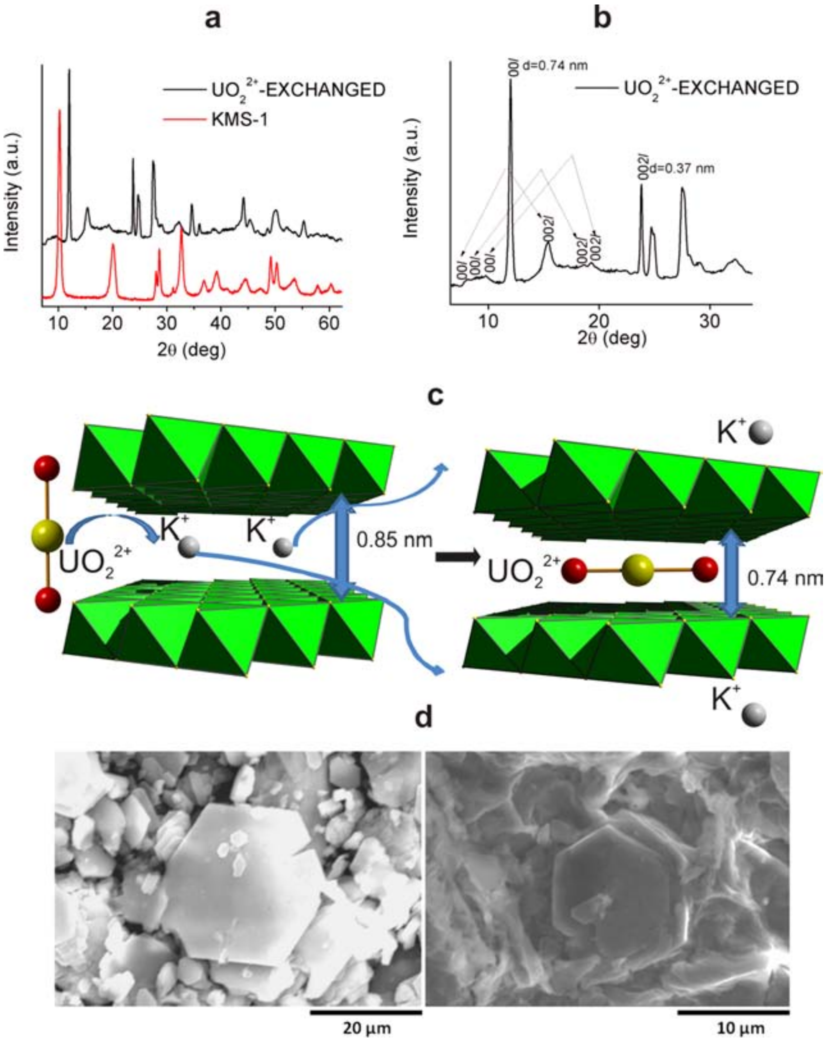


Figure 1. (a) X-ray powder diffraction patterns for the pristine $K_{2x}Mn_xSn_{3-x}S_6$ (x = 0.5−0.95) and UO_2^{2+}-exchanged product. (b) A part of the XRD pattern of the UO_2^{2+}-exchanged product with the indication of the Bragg 00*l*, 002*l* peaks of the various layered phases. (c) Schematic of the intercalative mechanism of capture of UO_2^{2+} ions by KMS-1 through exchange of its interlayer potassium cations. The green polyhedra represent $(Mn,Sn)S_6$ octahedral units. (d) SEM images of the crystallites of the pristine (left) and UO^{2+}-exchanged (right) KMS-1.

determined accurately by inductively coupled plasma-atomic emission (ICP-AES) analysis on the exchanged material was 1:1:2.

The distribution coefficient K_d, used for the determination of the affinity and selectivity of compounds KMS-1 for UO_2^{2+}, is given by the equation $K_d = (V[(C_0 - C_f)/C_f])/m$, 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]

The UO_2^{2+} uptake from solutions of various concentrations (33−400 ppm, pH ~3.5) was studied by the batch method at V:m ~ 1000 mL/g, room temperature, and 12 h contact. These data were used for the determination of UO_2^{2+} sorption isotherms.

The competitive ion exchange experiments of KMS-1 were also carried out with the batch method at V:m ratio 1000 mL/g, room temperature, and 12 h contact.

Ion-Exchange Studies with Contaminated Potable, Lake and Seawater and Original Seawater. The intentionally contaminated samples were prepared by diluting appropriate microliter amounts of U (~1000 ppm) commercial solutions with drinking, lake, or seawater. For each experiment, a total of 50−100 mg of compound KMS-1 was weighted into a 20 mL glass vial. A 5 mL sample of water solution was added to each vial and the mixture was kept under magnetic stirring for ~12 h. The suspension from the reaction was filtered (through filter paper, Whatman No. 1) and the filtrate was analyzed for its uranium content with inductively coupled plasma-mass spectroscopy (ICP-MS).

Kinetic Studies. UO_2^{2+} ion-exchange experiments of various reaction times (2, 5, 15, 30, 60, 120 min) have been performed. For each experiment, a total of 10−50 mg of KMS-1 was weighted into a 20 mL glass vial. A 5−10 mL sample of water containing UO_2^{2+} ([U] ~ 0.04−1 ppm) 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 uranium content with ICP-MS.

Regeneration. Samples of ~30 mg of UO_2^{2+}-laden compounds were treated for ~12 h with ~10 mL solutions containing 2 M Na_2CO_3. After this treatment, the samples were analyzed for their U content with ICP-AES.

■ RESULTS AND DISCUSSION

The ion-exchange of KMS-1 with UO_2^{2+} can be rapidly accomplished, accompanied by a color darkening of KMS-1. It is described with the following equation:

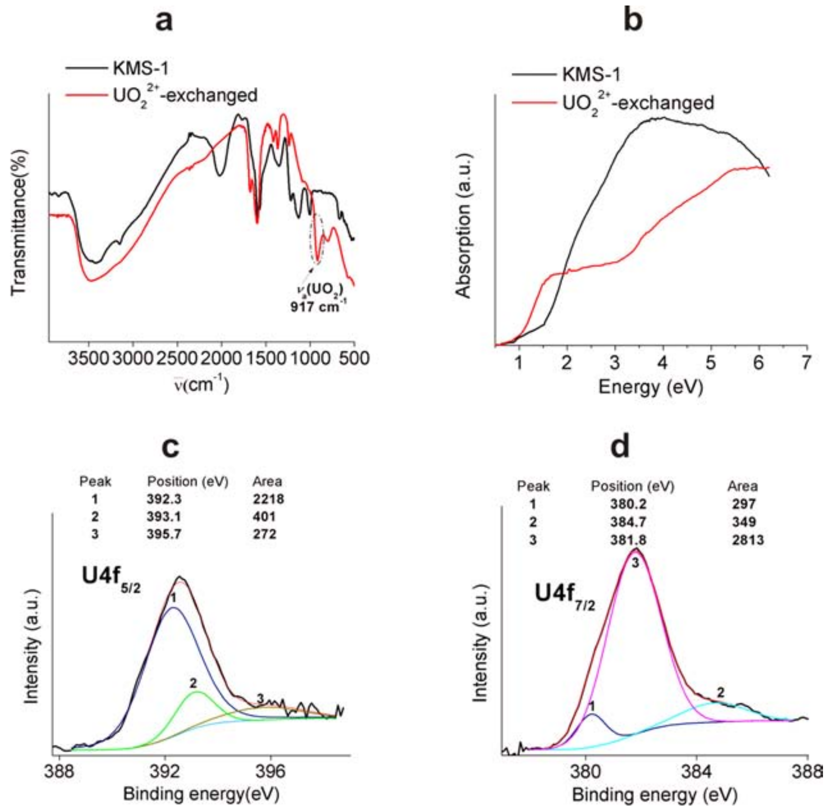


Figure 2. (a) Mid-IR spectra of KMS-1 and the UO_2^{2+}-exchanged compound. The peak corresponding to the antisymmetric vibration of the O═U^{VI}═O group is highlighted with a circle. (b) Solid-state NIR−UV−vis spectra for pristine KMS-1 and UO_2^{2+}-exchanged material. (c) U4f$_{5/2}$ and (d) U4f$_{7/2}$ spectra with the deconvolution of the corresponding XPS peaks into three components.

$$K_{1.9}Mn_{0.95}Sn_{2.05}S_6 + 0.95UO_2(NO_3)_2 \xrightarrow[25\,°C,12\,h]{H_2O\,(pH\sim3.5)} [UO_2(H_2O)_y]_{0.95}[Mn_{0.95}Sn_{2.05}S_6] + 1.9KNO_3$$

The complete exchange of K^+ ions by UO_2^{2+} was confirmed by ICP-AES and energy dispersive spectroscopy (EDS). These analytical data showed the expected ratio U:Mn:Sn:S ∼ 1:1:2:6 for the fully exchanged material. Powder X-ray diffraction (PXRD) data (Figure 1a) showed the presence of a mixture of layered phases, which are mainly due to differently hydrated UO_2^{2+} species in the interlayer space. One of these phases exhibits an interlayer spacing (d_{00l}) of ∼7.4 Å, which is 1.2 Å smaller than that of the KMS-1. Interestingly, this contraction of the interlayer space is close to the difference between the diameters of U^{6+} (∼1.4−1.8 Å) and K^+ (∼3.0−3.2 Å). Therefore, the phase with the interlayer spacing of ∼7.4 Å may contain the linear nonhydrated $[O{=}U{=}O]^{2+}$ cation ordering parallel to the layer plane (Figure 1b,c). Scanning electron microscopy (SEM) indicated that UO^{2+}-exchanged KMS-1 retained the hexagonal platelike shape of the crystallites of the pristine KMS-1 (Figure 1d). Thermogravimetric analysis (TGA) for the uranyl-exchanged material revealed a total weight loss of ∼12% from 25 to 300 °C (Figure S1, Supporting Information), which is attributed to the removal of ∼5.5 water molecules per formula of the compound. The presence of uranyl cation in the exchanged material was further demonstrated by infrared (IR), solid-state NIR−UV−vis, and X-ray photoelectron spectroscopy (XPS). The IR spectrum of the exchanged material (Figure 2a) showed the existence of a strong peak at ∼917 cm^{-1} (not present in the spectrum of KMS-1) assigned to the antisymmetric vibration of the $[O{=}U^{VI}{=}O]^{2+}$ group, which is significantly red-shifted compared to the corresponding peak for the aqueous UO_2^{2+} complexes (∼963 cm^{-1}).[23] The solid-state UV−vis reflectance spectrum of the UO_2^{2+}-exchanged material contains a broad feature between 3 and 6 eV and a relatively sharp absorption edge with an onset at 0.95 eV (Figure 2b). This low-energy optical absorption may explain the darker color of the uranyl-exchanged material compared to that of KMS-1, showing band gap energy of ∼1.3 eV. Note that the solid-state NIR−UV−vis spectrum of $Cs_4(UO_2)(S_2)_3$, a mononuclear compound with UO_2−S_2 covalent bonds, also shows an optical absorption with an onset at ∼0.95 eV.[24] This feature was assigned as a charge transfer from a mainly sulfur p orbital to a primarily uranium 6d/5f orbital. XPS data revealed the presence of U4f$_{5/2}$ and U4f$_{7/2}$ peaks, with their main components corresponding to binding energies of 392.3 (peak 1, Figure 2c) and 381.8 eV (peak 3, Figure 2d). These binding energies are consistent with U^{6+}.[23]

To evaluate the ability of KMS-1 to absorb UO_2^{2+}, we performed batch studies.[25] The uranyl ion exchange equilibrium data are graphed in Figure 3a. The best description of the data (see Supporting Information, Table S1 and Figure S2 for a more detailed discussion of the equilibrium data) is provided by the Langmuir model,[26] which is consistent with the formation of a monolayer of UO_2^{2+} ions in the interlayer space of KMS-1. The maximum exchange capacity (q_m) of KMS-1 and its distribution coefficient (K_d^U) values[26] were found to be 382(20) U mg/g and (1.1 × 10^4)−(1.8 × 10^5) mL/g respectively, which are well-comparable with those for the

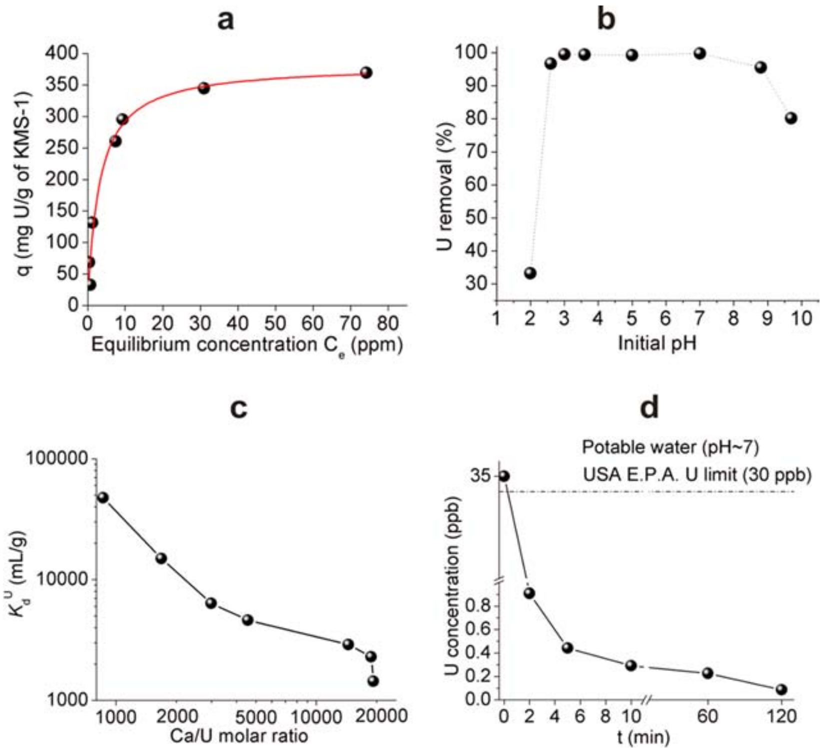


Figure 3. (a) Equilibrium data for UO_2^{2+} ion exchange (pH ~3.5, V:m = 1000 mL/g, contact time ~12 h, initial U concentrations in the range 33–400 ppm). The solid line represents the fitting of the data with the Langmuir model. (b) Variation of the UO_2^{2+} uptake by KMS-1 with pH (V:m = 1000 mL/g, contact time ~12 h, initial U concentration ~5 ppm). (c) The variation of the distribution coefficient K_d^U (mL/g) with the Ca:Cs molar ratio (pH ~3.5, V:m = 1000 mL/g, contact time ~12 h, initial U concentration ~4.25 ppm). The line is only a guide for the eye. (d) The kinetics of UO_2^{2+} ion-exchange of KMS-1 for potable water solutions with initial U concentration ~35 ppb, pH ~7, V:m = 100 mL/g. The line is only a guide for the eye.

Table 1. Selected Results for the Ion-Exchange of KMS-1 with UO_2^{2+}-Containing Water Samples

			U concn (ppb)		
sample	pH	V:m(mL/g)	initial	final[a]	% removal
distilled water (0.34 M NaCl)	3	1000	2500	12–22	99.1–99.5
distilled water (0.15 M $NaNO_3$)	6.5	1000	3250	103–128	96.1–96.8
potable water[b]	7	100	36	0.5–0.7	98.1–98.6
Lake Michigan water[c]	7.3	100	34.2	0.9–1.1	96.8–97.4
contaminated seawater (Gulf of Mexico)	8.2	16–50	1308	1.2–6.5	99.5–99.9
contaminated seawater[d] (Pacific ocean)	8.2	20–50	1278	1.1–2.0	99.8–99.9
contaminated seawater (Gulf of Mexico)	8.2	100	39	5.3–8.5	78.3–86.5
original seawater[e] (Gulf of Mexico)	8.2	100	3.8	0.6–0.9	76.3–84.2

[a] Range of concentrations obtained from three different experiments. [b] Potable water as found in Evanston, IL, contains 10.7 ppm of Na^+, 32.9 ppm Ca^{2+}, 8.5 ppm Mg^{2+}, 7 ppm K^+, and other ions of insignificant concentrations. [c] Water samples from Lake Michigan (Evanston, IL) contain 20 ppm of Na^+, 24 ppm Ca^{2+}, 8.8 ppm Mg^{2+}, 2.7 ppm K^+, and other ions of insignificant concentrations. [d] The cations with the highest concentrations in these seawater samples were Na^+ (8557 ppm), Mg^{2+} (820 ppm), K^+ (500 ppm), and Ca^{2+} (262 ppm). [e] The cations with the highest concentrations in these seawater samples were Na^+ (9486 ppm), Mg^{2+} (897 ppm), K^+ (556 ppm), and Ca^{2+} (274 ppm).

best UO_2^{2+} sorbents.[2−4,14] The value of the Langmuir constant (b, an indicator of the affinity and selectivity of a sorbent for an ion) for the UO_2^{2+}exchange was 79(17) L/mmol, which is substantially larger than the b values for the Sr^{2+} [39(5) L/mmol)] and Cs^+ [9.3(1) L/mmol] exchange of KMS-1.[20,21]

KMS-1 (in its Na^+ form) can be easily regenerated by treating the UO_2^{2+}-laden product with a concentrated Na_2CO_3 solution (2 M, pH ~10), and the material retained its layered structure (Figure S3, Supporting Information). The regenerated samples showed exchange capacities of ~120–190 mg/g, which are high but significantly lower than the capacities of pristine KMS-1 samples (~380 mg/g). However, these high capacities (120–190 mg/g) of regenerated KMS-1 were retained even after (at least) six cycles of regeneration/reuse experiments.

Ion exchange reactions of KMS-1 performed with UO_2^{2+} solutions ([U] ~ 5 ppm) of various pH values (2–10) showed that the percentage of uranium removal remained very high (≥95%) in a wide pH range (2.5–9) and remains significant (~80%) even at pH ~10 (Figure 3b). Compared to oxidic ion exchangers (e.g., zeolites,[27] manganese oxides[2] etc.), KMS-1 shows better performance under acidic conditions (typically oxidic ion exchangers are active for pH >4). The KMS-1 contains soft basic sites, the S^{2-} ligands, which display small affinity for hard proton ions. Instead, the UO_2^{2+} exchange of the majority of oxygen-containing materials strongly interferes with proton ions having high affinity for the hard O^{2-} ligands. It is also interesting that KMS-1 was very efficient in capturing UO_2^{2+} at pH ≥7, where there are mainly anionic forms of UO_2^{2+} [e.g., $UO_2(CO_3)_3^{4-}$].[1]

We also tested the performance of KMS-1 in the presence of a large excess of Na^+, since very high sodium concentrations are usually present in wastewater. We have observed an exceptional ability of KMS-1 to absorb UO_2^{2+} quantitatively (≥96% U removal capacity) in the presence of a tremendous ($\geq 10^4$-fold) excess of NaCl or $NaNO_3$ (Table 1), which indicates the very high selectivity of KMS-1 for UO_2^{2+} against Na^+.

Ca^{2+} ions also may exist in relatively high concentrations in wastewater and usually constitute strong competitors for the ion exchange of toxic ions. Therefore, the effect of $CaCl_2$ on the UO_2^{2+}-sorption properties of KMS-1 was also investigated. KMS-1 showed a remarkably high tolerance of its UO_2^{2+}-sorption capacity on the Ca^{2+} competition. For example, it can been seen that very high removal capacities (~94–98%) and excellent K_d^U values [$(1.5\text{–}4.8) \times 10^4$ mL/g] were obtained at very large $CaCl_2$:U molar ratios [$(8.6 \times 10^2)\text{–}(1.7 \times 10^3)$] (Figure 3c). It is interesting that even with a tremendous excess of $CaCl_2$ ($CaCl_2$:U molar ratio $\sim 1.5\text{–}1.9 \times 10^4$) KMS-1 retained a very good UO_2^{2+} removal efficiency (60–74%) and high K_d^U values [$(1.4\text{–}2.9) \times 10^3$ mL/g]. Furthermore, a huge $K_{UO_2^{2+}/Ca^{2+}}$ selectivity coefficient[28] of $\sim 6.2 \times 10^4$ was found (see the Supporting Information and Figure S4), indicating an exceptional selectivity of KMS-1 for UO_2^{2+} against Ca^{2+}. Such a preference of KMS-1 for UO_2^{2+} in the presence of high Ca^{2+} concentrations indicates strong covalent $UO_2^{2+}\cdots S^{2-}$ bonding interactions, in accordance with the spectroscopic data for the UO_2^{2+}-exchanged material (see above).

Because of the excellent UO_2^{2+}-exchange properties described above, we decided to examine the applicability of KMS-1 for remediation of real world water samples intentionally contaminated by trace concentrations of UO_2^{2+} ([U] ~ 0.04–1 ppm). Selected results are shown in Table 1. Initially, we examined the performance of KMS-1 for decontamination of potable water solutions [pH ~7, volume (*V*) of solution to mass (*m*) of ion exchanger (*V*:*m*) = 100 mL/g] to which ppb levels of U (~35 ppb) were added. The removal of such low U levels was found to be quantitative (>98–99%). The kinetics of this process was also investigated. It can be seen (Figure 3d) that the sorption of UO_2^{2+} by KMS-1 is very fast and the final U concentration becomes less than 1 ppb [i.e., well-below the acceptable limit of 30 ppb defined by the US Environmental Protection Agency (EPA) for uranium in potable water] with only 2 min treatment of the solution with KMS-1. We also tested the capability of KMS-1 to remediate lake water (Lake Michigan) intentionally contaminated by traces of U (34 ppb). The material performed similarly as for the potable water samples, eliminating the U content of the initial solutions.

The most challenging experiments we performed were with seawater samples (Gulf of Mexico and Pacific Ocean). Specifically, such samples were spiked with ~1.2–1.3 ppm of U. Then, ion-exchange reactions of KMS-1 with these solutions were performed (*V*:*m* ~ 50 mL/g). Almost 100% UO_2^{2+} removal capacities were achieved, and excellent distribution coefficients of $(2\text{–}3) \times 10^4$ mL/g were obtained. The quantitative sorption of the uranium of these solutions by KMS-1 was also confirmed by the ICP-MS analysis of the U content of the solid exchanged materials digested in concentrated acid. Furthermore, reactions were performed with seawater solutions to which ppb levels of U (~39 ppb) were added. Again, KMS-1 showed high removal capacities in the range 78–86% (*V*:*m* = 100 mL/g). Finally, we tested the ability of KMS-1 to absorb the naturally occurring U (~3.8 ppb for the samples tested) of seawater. The results obtained indicate a remarkable efficiency of KMS-1 to remove this extremely low level U (removal capacities ~84%, *V*:*m* = 100 mL/g) and are encouraging for the use of KMS-1 for sequestering U from seawater.[29] The ability of KMS-1 to absorb uranium from seawater is the highest reported.[30]

■ CONCLUSIONS

In conclusion, we demonstrated that the ion-exchange layered metal sulfide KMS-1 shows a remarkably high exchange capacity, affinity, and selectivity for UO_2^{2+} ions, which seems to be the result of strong $UO_2^{2+}\cdots S^{2-}$ bonding interactions. Given the observed exceptional selectivity of the layered sulfide KMS-1 for UO_2^{2+} and against hard cations (Na^+, Ca^{2+}), our investigations indicate UO_2^{2+} as a rather soft cation preferentially sorbed by a material with soft ligands, in contrast to the general view of this ion as a typical hard acid. We should also note that KMS-1 is very effective for decontamination of real world water samples from trace levels of U. KMS-1 is (a) inexpensive, (b) very stable in the atmosphere and water, (c) highly selective for UO_2^{2+} with very fast sorption kinetics, (d) easily regenerated with a cost-affordable and environmentally friendly method, and (e) reusable several times as UO_2^{2+}-exchanger. Thus, it represents one of the most promising sorbents for efficient and cost-effective treatment of wastes and groundwater containing highly toxic U levels. All prior efforts to remove or recover uranium from water have been focused on oxidic organic or inorganic materials under the hypothesis that the $[UO_2]^{2+}$ ion is a hard Lewis acid ion. Our work shows that this may be an oversimplified assumption and that the $[UO_2]^{2+}$ ion is much softer than previously thought. This changes the way we think about the $[UO_2]^{2+}$ ion and could open the path to more effective approaches toward its capture, such as the one shown here. Finally, the ability of KMS-1 to efficiently absorb the naturally occurring U of seawater points to the potential application of this material for uranium harvesting from the sea.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details about the characterization and analytical techniques used, as well as Figures S1–S4 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

m-kanatzidis@northwestern.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Science Foundation (DMR-1104965) is gratefully acknowledged. This work made use of the facilities in the Integrated Molecular Structure Education and Research Center (IMSERC) at the Northwestern University. A description of the facility and full funding disclosure can be found at http://pyrite.chem.northwestern.

edu/analyticalserviceslab/asl.htm. This material is based upon work supported by IEC. We also thank Mr. Collin Morris and Dr. Danielle Gray for providing us seawater samples from Gulf of Mexico and Pacific Ocean, respectively.

■ REFERENCES

(1) Craft, E. S.; Abu-Qare, A. W.; Flaherty, M. M.; Garofolo, M. C.; Rincavage, H. L.; Abou-Donia, M. B. *J. Toxicol. Envon. Health B* **2004**, *7*, 297−317.

(2) Al-Attar, L.; Dyer, A. *J. Mater. Chem.* **2002**, *12*, 1381−1386.

(3) Chiarizia, R.; Horwitz, E. P.; Alexandratos, S. D.; Gula, M. J. *Sep. Sci. Technol.* **1997**, *32*, 1−35.

(4) Fryxell, G. E.; Lin, Y. H.; Fiskum, S.; Birnbaum, J. C.; Wu, H.; Kemner, K.; Kelly, S. *Environ. Sci. Technol.* **2005**, *39*, 1324−1331.

(5) Mellah, A.; Chegrouche, S.; Barkat, M. *J. Colloid Interface Sci.* **2006**, *296*, 434−441.

(6) Webb, S. M.; Fuller, C. C.; Tebo, B. M.; Bargar, J. R. *Environ. Sci. Technol.* **2006**, *40*, 771−777.

(7) Jang, J. H.; Dempsey, B. A.; Burgos, W. D. *Environ. Sci. Technol.* **2007**, *41*, 4305−4310.

(8) Cantrell, K. J.; Kaplan, D. I.; Wietsma, T. W. *J. Hazard. Mater.* **1995**, *42*, 201−212.

(9) Fiedor, J. N.; Bostick, W. D.; Jarabek, R. J.; Farrell, J. *Environ. Sci. Technol.* **1998**, *32*, 1466−1473.

(10) Gu, B. H.; Wu, W. M.; Ginder-Vogel, M. A.; Yan, H.; Fields, M. W.; Zhou, J.; Fendorf, S.; Criddle, C. S.; Jardine, P. M. *Environ. Sci. Technol.* **2005**, *39*, 4841−4847.

(11) Dushenkov, S.; Vasudev, D.; Kapulnik, Y.; Gleba, D.; Fleisher, D.; Ting, K. C.; Ensley, B. *Environ. Sci. Technol.* **1997**, *31*, 3468−3474.

(12) Scott, T. B.; Tort, O. R.; Allen, G. C. *Geochim. Cosmochim. Acta* **2007**, *71*, 5044−5053.

(13) McKinley, J. P.; Zachara, J. M.; Smith, S. C.; Turner, G. D. *Clays Clay Miner.* **1995**, *43*, 586−598.

(14) Sharma, P.; Tomar, R. *Microporous Mesoporous Mater.* **2008**, *116*, 641−652.

(15) Marinin, D. V.; Brown, G. N. *Waste Manage.* **2000**, *20*, 545−553.

(16) Pearson, R. G. *Science* **1966**, *151*, 172−177.

(17) Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 7901−7902.

(18) Wersin, P.; Hochella, M. F.; Persson, P.; Redden, G.; Leckie, J. O.; Harris, D. W. *Geochim. Cosmochim. Acta* **1994**, *58*, 2829−2843.

(19) Descostes, M.; Schlegel, M. L.; Eglizaud, N.; Descamps, F.; Miserque, F.; Simoni, E. *Geochim. Cosmochim. Acta* **2010**, *74*, 1551−1562.

(20) Manos, M. J.; Ding, N.; Kanatzidis, M. G. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 3696−3699.

(21) Manos, M. J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 6599−6607.

(22) (a) Manos, M. J.; Kanatzidis, M. G. *Chem.—Eur. J.* **2009**, *15*, 4779−4784. (b) Manos, M. J.; Malliakas, C. D.; Kanatzidis, M. G. *Chem.—Eur. J.* **2007**, *13*, 51−58. (c) Manos, M. J.; Petkov, V. G.; Kanatzidis, M. G. *Advanced Functional Materials* **2009**, *19*, 1087−1092.

(23) Amayri, S.; Arnold, T.; Reich, T.; Foerstendorf, H.; Geipel, G.; Bernhard, G.; Massanek, A. *Environ. Sci. Technol.* **2004**, *38*, 6032−6036.

(24) Sutorik, A. C.; Kanatzidis, M. G. *Polyhedron* **1997**, *16*, 3921−3927.

(25) Wachinski, A. M.; Etzel, J. E. *Environmental Ion Exchange: Principles and Design*; CRC Press: Boca Raton, FL, 1997.

(26) Do, D. D. In *Adsorption Analysis:Equilibria and Kinetics*; Imperial College Press: London, 1998; pp 13−17, 49−57.

(27) Amini, S.; Dyer, A. *J. Radioanal. Nucl. Chem.* **1994**, *178*, 273−289.

(28) Dyer, A.; Pillinger, M.; Newton, J.; Harjula, R.; Moller, T.; Amin, S. *Chem. Mater.* **2000**, *12*, 3798−3804.

(29) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Nature* **1979**, *280*, 665−666.

(30) Egawa, H.; Nonaka, T.; Abe, S.; Nakayama, M. *J. Appl. Polym. Sci.* **1992**, *45*, 837−841.