

Rapid Simultaneous Removal of Toxic Anions $[\text{HSeO}_3]^-$, $[\text{SeO}_3]^{2-}$, and $[\text{SeO}_4]^{2-}$, and Metals Hg^{2+} , Cu^{2+} , and Cd^{2+} by MoS_4^{2-} Intercalated Layered Double Hydroxide

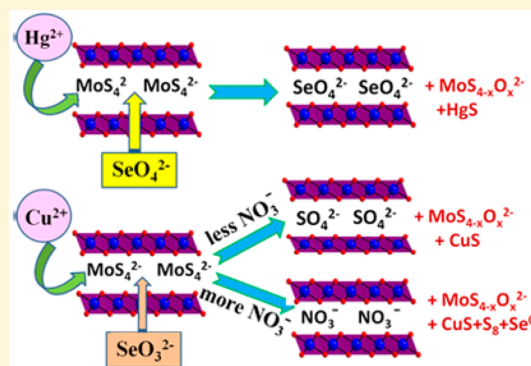
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S Supporting Information

ABSTRACT: We demonstrate fast, highly efficient concurrent removal of toxic oxoanions of Se(VI) (SeO_4^{2-}) and Se(IV) ($\text{SeO}_3^{2-}/\text{HSeO}_3^-$) and heavy metal ions of Hg^{2+} , Cu^{2+} , and Cd^{2+} by the MoS_4^{2-} intercalated Mg/Al layered double hydroxide (MgAl- MoS_4 -LDH, abbr. MoS_4 -LDH). Using the MoS_4 -LDH as a sorbent, we observe that the presence of Hg^{2+} ions greatly promotes the capture of SeO_4^{2-} , while the three metal ions (Hg^{2+} , Cu^{2+} , Cd^{2+}) enable a remarkable improvement in the removal of $\text{SeO}_3^{2-}/\text{HSeO}_3^-$. For the pair Se(VI)+ Hg^{2+} , the MoS_4 -LDH exhibits outstanding removal rates (>99.9%) for both Hg^{2+} and Se(VI), compared to 81% removal for SeO_4^{2-} alone. For individual SeO_3^{2-} (without metal ions), 99.1% Se(IV) removal is achieved, while $\geq 99.9\%$ removals are reached in the presence of Hg^{2+} , Cu^{2+} , and Cd^{2+} . Simultaneously, the removal rates for these metal ions are also >99.9%, and nearly all concentrations of the elements can be reduced to <10 ppb, a limit acceptable for drinking water. The maximum sorption capacities for individual Se(VI) and Se(IV) are 85 and 294 mg/g, respectively. The 294 mg/g capacity for Se(IV) reaches a record value, placing the MoS_4 -LDH among the highest-capacity selenite adsorbing materials described to date. More interestingly, the presence of metal ions extremely accelerates the capture of the selenium oxoanions because of the reactions of the metal ions with the interlayer MoS_4^{2-} anions. The sorptions of Se(VI)+Hg and Se(IV)+M (M = Hg^{2+} , Cu^{2+} , Cd^{2+}) are exceptionally rapid, showing >99.5% removals for Hg^{2+} within 1 min and ~99.0% removal for Se(VI) within 30 min, as well as >99.5% removals for pairs Cu^{2+} and Se(IV) within 10 min, and Cd^{2+} and Se(IV) within 30 min. During the sorption of $\text{SeO}_3^{2-}/\text{HSeO}_3^-$, reduction of Se(IV) occurs to Se^0 caused by the S^{2-} sites in MoS_4^{2-} . Sorption kinetics for the oxoanions follows a pseudo-second-order model consistent with chemisorption. The intercalated material of MoS_4 -LDH is very promising as a highly effective filter for decontamination of water with toxic Se(IV)/Se(VI) oxoanions along with heavy metals such as Hg^{2+} , Cd^{2+} , and Cu^{2+} .



INTRODUCTION

Selenium is an essential nutrient element for humans and animals in trace amounts,¹ while it is extremely toxic at higher concentrations.^{2,3} It has the narrowest range between dietary deficiency (<40 $\mu\text{g}/\text{day}$) and toxic levels (>400 $\mu\text{g}/\text{day}$),⁴ and problems of both Se toxicity and deficiency occur in different parts all over the world.^{5,6} In particular, the redox-sensitive radionuclide of ^{79}Se has a very long half-life ($t_{1/2} \approx 3.27 \times 10^5$ years⁷) and is chemically and radiologically toxic.⁸ Acute exposure to selenium compounds may lead to severe respiratory problems and neurological effects.⁹ In drinking water, 40 and 50 ppb have been set as the maximum acceptable concentration by the World Health Organization (WHO)¹⁰ and United States Environmental Protection Agency (USEPA),¹¹ and in Europe and Japan the limit is 10 ppb.¹²

Removal of water-borne selenium has attracted increasing attention.^{13–15} Selenium contaminants have been normally generated from coal-fire power plants and mining and metal smelting industries. The treatment of selenium-contaminated water is challenging. Selenium mobility and toxicity are strongly dependent on its redox state,^{16,17} from highly soluble oxoanions selenate (Se(VI), SeO_4^{2-}), selenite (Se(IV), SeO_3^{2-}), and hydroselenite (Se(IV), HSeO_3^-), to elemental Se(0) and solid or gaseous selenide ($\text{Se}(-\text{II})$).¹⁸ Se immobilization in the environment occurs normally via chemical reduction to insoluble Se(0).^{8,19}

On the other hand, water contamination by heavy metals such as Hg^{2+} , Cd^{2+} , and Cu^{2+} is becoming an increasingly

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important issue in separation science and environmental remediation,^{20–26} because of the severe harm to human beings, animals, and other species.^{27–29} Mercury (Hg), as one of the most toxic elements, exhibits its persistence and bioaccumulation in the food chain and thus becomes a severe environmental problem.³⁰ Hg contamination in aquatic systems is extremely harmful to both public health and aquatic life. Thus, the removal of such toxic metal ions from water sources which generally also contain other toxic elements including selenium is an important environmental challenge.

Various treatment technologies have been used for water contaminated by toxic oxoanions and metal cations, including chemical precipitation, adsorption, ion-exchange, filtration, and so on.^{31–35} Adsorption is highly effective and economical because of its low cost, simple design, and strong sorption functionality. Adsorption and heterogeneous reduction on iron, alumina, titanium oxides, and so on can retard the migration of selenium in the environment.^{19,36–38} Nanomagnetite particles appeared as promising sorbents for the removal of selenite from aqueous solutions.¹⁹ At low Se (IV) concentrations, the nanomagnetites reduce Se(IV) to Se(–II) followed by a subsequent precipitation of highly insoluble FeSe.¹⁹ Farha and co-workers developed zirconium-based metal–organic framework (MOF; NU-1000) showing high adsorption capacity and fast uptake toward selenate and selenite, making use of the large MOF apertures and labile Zr(IV) coordination sites.¹³ Carbon nanotubes, nanospheres, and graphene oxide composites have been utilized to trap selenium^{39,40} and mercury;⁴¹ however, these materials are cost prohibitive, thus limiting their application.

Layered double hydroxides (LDHs) and layered rare earth hydroxides (LRHs) are two kinds of important two-dimensional materials consisting of positively charged host layers and counter-anions in the interlayer space. Their excellent intercalation and anion-exchange capability⁴² allow them to play versatile roles on applications such as two-dimensional nanoreactors,⁴³ sorbents and scavengers.^{44–47} The anion-exchange capability (layer –OH groups and interlayer anions) of the LDH materials enables them to be used for the capture of toxic oxoanions.^{14,15,48,49} Very recently, Wang et al. reported efficient uptake of selenite and selenate anions using a cationic layered rare earth hydroxide compound, with high sorption capacities of 207 and 124 mg/g, for selenite and selenate, respectively.⁵⁰

When the classical anions in the LDH galleries are exchanged with thioanions, the materials become functionalized toward the effective capture of heavy toxic cations because of selective M–S bonding. Previously, we introduced polysulfide $[S_x]^{2-}$ ^{51–54} and MoS_4^{2-} ^{55,56} anions into the LDH galleries, to form S_x -LDH and MoS_4 -LDH which display effective capture for heavy metals.^{51,53,55} We recently demonstrated the excellent removal and selectivity of the MoS_4 -LDH toward toxic oxoanions of As(III), As(V), and Cr(VI).⁵⁶ The selenium oxoanions are more difficult to selectively remove from solution. In this work, we examined the efficacy of MoS_4 -LDH toward removing the selenium oxoanions and we discovered a surprising effect. The removal of these selenium oxoanions is strongly enhanced in the presence of soft Lewis acid metal ions. Herein, we demonstrate the excellent capability of the MoS_4 -LDH for simultaneous removals of toxic selenium oxoanions and the heavy metal ions (Hg^{2+} , Cu^{2+} , and Cd^{2+}). The three metal ions are all beneficial for the Se(IV) uptake, and Hg^{2+} is particularly effective for the Se(VI) capture. The concentrations of Se and

metal ions can be rapidly reduced to extremely low values acceptable for drinking water, in virtue of the MoS_4^{2-} group of the MoS_4 -LDH.

■ EXPERIMENTAL SECTION

Materials. $MgAl$ - NO_3 -LDH was prepared by a NO_3^-/CO_3^{2-} anion-exchange reaction referring to previous work.⁴⁴ From the NO_3 -LDH, the MoS_4^{2-}/NO_3^- exchange was conducted to produce the MoS_4 -LDH, which had a chemical formula of $Mg_{0.66}Al_{0.34}(OH)_2(MoS_4)_{0.17} \cdot 0.8H_2O$ based on ICP and CHN analyses, as we previously reported.⁵⁵

Uptake of Oxoanions of Se(IV)/Se(VI) with Addition of Metal Ions of Hg^{2+} , Cu^{2+} , and Cd^{2+} . The sorption experiments of the MoS_4 -LDH for the Se(IV)/Se(VI) oxoanions and metal ions of Hg^{2+} , Cu^{2+} , and Cd^{2+} were performed at room temperature. Aqueous solutions of Se(IV)/Se(VI) oxoanions and metal ions of Hg^{2+} , Cu^{2+} and Cd^{2+} were prepared by dissolving their corresponding salts of Na_2SeO_3 , Na_2SeO_4 , $Hg(NO_3)_2$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$ in deionized water. The pH values were generally the local values when dissolving the salts at certain concentrations. For the mixtures of $SeO_3^{2-}/HSeO_3^-$ and metal ions, ~ 1 mol/L HNO_3 was added beforehand to avoid the hydrolysis of the metal ions due to the alkalinity of Na_2SeO_3 , thus slightly lower pHs were used (the metal ions may generate $M(OH)_2$ precipitates when contact with alkaline Na_2SeO_3). For the mixtures of oxoanions and metal ions, the molar ratios of Se and metal ions were selected $\sim 1:1$ or other values to check the effect of their relative quantity.

The uptake studies were carried out using a batch method by dispersing 0.03 g of MoS_4 -LDH into 30 mL ($V/m = 1000$ mL/g) of aqueous solutions in 50 mL polypropylene centrifuge tubes. After blending the previous solutions with the MoS_4 -LDH solid, the as-obtained suspensions in the centrifuge tubes were shaken in a mechanical shaker to ensure their enough contact. After 24 h contact, centrifugations were performed to separate the solutions for subsequent inductively coupled plasma (ICP) analysis. The adsorptive capacity was evaluated from the concentration difference in the initial and final solutions.

The distribution coefficient (K_d) in absorption experiments is defined by the equation of $K_d = (V[(C_0 - C_f)/C_f])/m$, where V is the solution volume (mL), C_0 and C_f are, respectively, the initial and final concentrations of elements (ppm, $\mu\text{g/mL}$), and m is the mass of the solid sorbent (g). The removal capacity, q_m (mg/g), that is, the adsorbed amount per unit mass of the sorbent, was calculated by using the expression of $q_m = 10^{-3} \times (C_0 - C_f) \times V/m$. The percent of removal was obtained from the equation of $100 \times (C_0 - C_f)/C_0$.

Maximum Uptake for Oxoanions of Se(IV) and Se(VI) with and without Metal Ions. The maximum uptakes of MoS_4 -LDH toward the oxoanions of Se(IV)/Se(VI) were performed by adding 0.03 g of MoS_4 -LDH into 30 mL of aqueous solutions with corresponding salts in 50 mL centrifuge tubes at varied elemental concentrations (10–500 ppm), being shaken in an oscillator for sufficient contact. Once an equilibrium was reached (~ 24 h), solutions and solid sorbents were separated by centrifugation, and ~ 10 mL of supernatants were taken out for ICP analyses. The data obtained were used for the determination of sorption isotherms. In order to check the difference of the maximum uptakes for Se with the presence of metal ions, sorption experiments were conducted with similar procedures by adding the metal ions at certain concentrations.

Sorption Kinetics for Se(IV)/Se(VI) with and without Metal Ions by MoS_4 -LDH and NO_3 -LDH. Sorption kinetic experiments of MoS_4 -LDH and NO_3 -LDH toward the elements were conducted under different contact time from 1 min to 24 h. For each operation, 0.03 g of the MoS_4 -LDH/ NO_3 -LDH solids was added into a 50 mL centrifugal tube, and 30 mL aqueous solutions containing ~ 10 ppm Se and/or equimolar metal ions were added ($V/m = 1000$ mL/g). At specified time intervals, the suspensions were centrifuged and ~ 4 mL of the supernatants were taken out for ICP analyses to get the concentrations of the elements.

Ion exchange reactions of $\text{SeO}_3^{2-}/\text{HSeO}_3^-$ and SeO_4^{2-} with NO_3^- -LDH. The exchange reactions of $\text{SeO}_3^{2-}/\text{HSeO}_3^-$ and SeO_4^{2-} with the NO_3^- of NO_3^- -LDH were conducted using 3-fold molar excess of the oxoanions relative to the containing NO_3^- in NO_3^- -LDH. In detail, to the suspension of 0.050 g NO_3^- -LDH in 10 mL water, 3-fold molar excess of the salt (0.051 g Na_2SeO_4 or 0.047 g Na_2SeO_3) was added and reacted for 24 or 48 h at room temperature. The resulting samples were filtered, washed with deionized water, and air-dried.

Selective Uptake Experiments toward Mixtures of As(III)/As(V)/Cr(VI)/Se(VI)/Se(IV) and $\text{Hg}^{2+}/\text{Cd}^{2+}/\text{Cu}^{2+}$. Considering the good sorption for the oxoanions of As(III)/As(V)/Cr(VI) using the MoS_4 -LDH,⁵⁶ all of the oxoanions of As(III)/As(V)/Cr(VI)/Se(VI)/Se(IV) and the metal ions of $\text{Hg}^{2+}/\text{Cd}^{2+}/\text{Cu}^{2+}$ were mixed together to see how the MoS_4 -LDH performed when they were all present in the solutions. The concentrations of the elements were at low concentrations of ~ 1 ppm for each. A amount of 0.03 g of the MoS_4 -LDH was put into the 30 mL aqueous solutions ($V/m = 1000$ mL/g). Other procedures were the same as above.

Physical Characterization and Chemical Analyses. Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nicolet-380 Fourier-transform infrared spectrometer using the KBr pellet method. X-ray diffraction (XRD) patterns of the as-prepared samples and those after the sorption experiments were collected using a PANalytical X'pert Pro MPD diffractometer with Cu K α radiation at room temperature, with step size of 0.0167° , scan time of 10 s per step, and 2θ ranging from 4.5 to 70° . The generator setting was 40 kV and 40 mA. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) measurements were carried out using a Hitachi S-4800 microscope. X-ray photoelectron spectroscopy (XPS) of the solid samples after the sorption experiments were performed using an ESCALAB 250Xi spectrometer (ThermoFisher). Fitting of the peaks was made by using the software Avantage.

The element concentrations in solutions before and after sorption were measured using ICP-AES (Jarrel-Ash, ICAP-9000). For determining the chemical compositions of the solid samples, nitric acid was first added to dissolve the solids (~ 0.005 g) followed by the ICP analysis.

RESULTS AND DISCUSSION

Removal of Se(IV)/Se(VI) Oxoanions with and without Metal Ions by MoS_4 -LDH at Low Concentrations. The Bragg (00 l) reflections and basal spacing (d_{basal}) of 1.05 nm (Figure 1a) are in good agreement with the reported values of the MoS_4 -LDH material.⁵⁵ XPS (Figure S1) was used to characterize the state of Mo and S in MoS_4 -LDH, which indicated the MoS_4^{2-} groups are stable during the intercalation. Concentrations of ~ 10 ppm for Se(IV) and Se(VI) were used. As known, the selenate species at pH > 2 are SeO_4^{2-} , while the

selenite at pH 5 is HSeO_3^- ; at pH = 7, two species of HSeO_3^- and SeO_3^{2-} coexist; and at pH = 8.5, the distribution of selenium species is $\sim 40\%$ HSeO_3^- and $\sim 60\%$ SeO_3^{2-} .¹⁴ In the current pH values of 3.0–8.8, the anions of Na_2SeO_4 would be SeO_4^{2-} , while for Na_2SeO_3 , two forms of HSeO_3^- and SeO_3^{2-} may coexist. The metal ions were set in equimolar ratios to Se. The affinity of MoS_4 -LDH for the constituents can be expressed in terms of the distribution coefficient K_d . Table 1 summarizes the sorption results for individual oxoanions and the mixtures. Without metal ions present, the sorption efficiency for Se(VI) seems relatively poor, giving a low removal of 81%, and the removal for Se(IV) is 99.1% at 24 h contact. The larger removal rate for Se(IV) may be due to a reduction reaction between the interlayer MoS_4^{2-} and the introduced $\text{SeO}_3^{2-}/\text{HSeO}_3^-$, which will be discussed below. Interestingly, when the metal ions were present, significantly enhanced sorptions for both Se(IV) and Se(VI) were displayed. For example, when Hg^{2+} was attendant, the Se(VI) uptake got extremely high, reaching a 99.95% removal, and the Se(VI) concentration can be reduced to 5 ppb (from 11 ppm), far below the limit value for drinking water based on WHO (40 ppb).¹⁰ Meanwhile, the Hg^{2+} concentration was simultaneously reduced to an extremely lower value of 1 ppb (from 21 ppm), lower than the permitted Hg^{2+} level for drinking water.⁵⁷ Though the Se(VI) removals with Cu^{2+} and Cd^{2+} present were not as effective as with Hg^{2+} , >92% Se(VI) removals can still be achieved. For Se(IV), all three metal ions (Hg^{2+} , Cd^{2+} , and Cu^{2+}) were very effective for the synergistic capture. For the pair Se(IV)+ Hg^{2+} , the concentrations were decreased to 8 ppb Se(IV) and 8 ppb Hg^{2+} from an initial ~ 10 ppm. The pairs Se(IV)+ Cu^{2+} and Se(IV)+ Cd^{2+} revealed similar results, giving ppb levels of ion concentrations lower than permitted values for drinking water (for Cd^{2+} the limit is 3–5 ppb⁵⁸). Nearly all removal rates were >99.8% and K_d values were $>10^5$ mL/g. Moreover, Cu^{2+} ions displayed the best efficiency for trapping Se(IV), with K_d values $>10^6$ mL/g for both Se(IV) and Cu^{2+} . This suggests that the low-cost Cu^{2+} can be used to assist the capture of Se(IV) which is relatively difficult to remove.

Typically, materials with K_d values of $>10^4$ mL/g are considered to be exceptional sorbents.^{53,59,60} As shown in Table 1, in the presence of the three metal ions, the K_d values for Se(IV)/Se(VI) are all 10^4 – 10^6 mL/g, displaying excellent uptake ability. The above results highlight the strong potential of the MoS_4 -LDH material as a highly effective filter for decontamination of water containing these pollutants. It also suggests the use of inexpensive and non toxic Cu^{2+} to improve the capture of selenate and selenite especially selenite.

Maximum Uptake Capacity (q_m) for Se(IV)/Se(VI) Oxoanions with or without Metal Ions. Maximum sorption capacities for the selenium oxoanions with and without metal ions were determined with sorption isotherms studies (Tables 2–5). The uptakes for the oxoanions by MoS_4 -LDH were observed to increase successively with increasing Se concentrations. ICP measurements revealed plenty of Mo existed in the filtrates after sorptions, and the released Mo was found to increase, suggesting ion exchange with the selenium oxoanions. The color of the solutions after sorptions became gradually darker (Figure S2A), and UV–visible absorption spectroscopy verified the presence of MoS_4^{2-} (absorption bands at 241, 317, and 468 nm (Figure S2B)).

For individual Se(VI), the sorption reached saturation at ~ 300 ppm (Table 2), giving a maximum capacity ~ 85 mg/g.

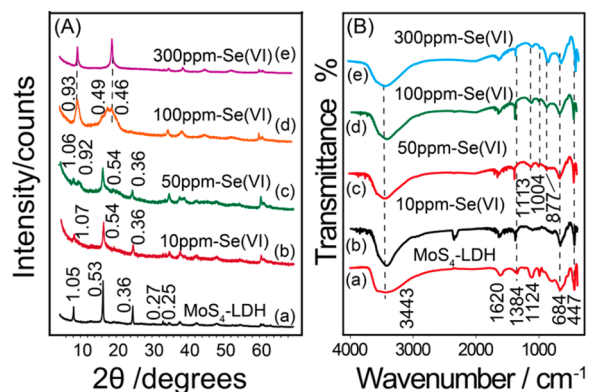


Figure 1. (A) XRD patterns and (B) IR spectra of samples after MoS_4 -LDH adsorbed SeO_4^{2-} and different concentrations.

Table 1. Removal Results of MoS₄-LDH toward Individual Se(IV)/Se(VI) Oxoanions and Mixtures with Metal Ions of Hg²⁺, Cu²⁺, and Cd²⁺^a

	C ₀ (ppm)	C _f (ppm)	removal (%)	K _d (mL/g)	q (mg/g)
Se(VI) ^b	Se: 9.92	1.85	81.35	4.4 × 10 ³	8.1
Se(VI)+Hg ²⁺ ^c	Se: 11.0	0.005	99.95	2.2 × 10 ⁶	11.0
	Hg: 21.0	0.001	99.99	2.1 × 10 ⁷	21.0
Se(VI)+Cu ²⁺ ^d	Se: 11.80	0.89	92.46	1.2 × 10 ⁴	10.9
	Cu: 8.13	0.26	96.80	3.0 × 10 ⁴	7.9
Se(VI)+Cd ²⁺ ^e	Se: 11.6	0.50	95.69	2.2 × 10 ⁴	11.1
	Cd: 14.5	0.53	96.34	2.6 × 10 ⁴	14.0
Se(IV) ^f	Se: 9.34	0.080	99.14	1.2 × 10 ⁵	9.3
Se(IV)+Hg ²⁺ ^g	Se: 6.40	0.008	99.88	8.0 × 10 ⁵	6.4
	Hg: 11.8	0.008	99.93	1.5 × 10 ⁶	11.8
Se(IV)+Cu ²⁺ ^h	Se: 9.96	0.003	99.96	2.8 × 10 ⁶	10.0
	Cu: 9.99	0.001	99.99	10.0 × 10 ⁶	10.0
Se(IV)+Cd ²⁺ ⁱ	Se: 9.66	0.014	99.86	6.9 × 10 ⁵	9.6
	Cd: 11.9	0.008	99.93	1.5 × 10 ⁶	11.9

^am = 0.03 g, V = 30 mL, V/m = 1000 mL/g; Contact time: 24 h. ^bpH values: 8.71 → 7.54. ^cpH values: 2.64 → 4.41. ^dpH values: 4.87 → 5.55. ^epH values: 4.93 → 6.17. ^fpH values: 8.57 → 6.29. ^gpH values: 2.36 → 4.18. ^hpH values: 6.10 → 6.03. ⁱpH values: 4.76 → 7.48.

Table 2. Sorption Data of MoS₄-LDH toward Se(VI) at Different Concentrations^a

C ₀ (ppm)	C _f (ppm)	removal (%)	q _e (mg/g)	C-Mo (ppm)
9.59 ^b	2.16	77.5	7.4	34.1
21.33 ^c	4.93	76.9	16.4	30.5
129 ^d	52.0	59.7	77	69.3
204 ^e	125	38.7	79	89.0
210 ^f	128	39.0	82	100.0
316 ^g	231	26.7	85	95.7

^am = 0.03 g, V = 30 mL, V/m = 1000 mL/g. Contact time: 24 h. ^bpH values: 8.71 → 7.54. ^cpH values: 8.79 → 7.45. ^dpH values: 7.90 → 6.85. ^epH values: 7.66 → 6.85. ^fpH values: 7.54 → 6.99. ^gpH values: 7.86 → 6.79. For 316 ppm Se(VI), the molar ratio of SeO₄²⁻ to MoS₄²⁻ in MoS₄-LDH is 2.59. Theoretical saturated concentration of Se(VI) (0.03 g MoS₄-LDH in 30 mL solution) is 122 ppm.

In this case we used 0.03 g MoS₄-LDH in a solution of 0.03 L, if assuming the Mo in the sorbent was completely dissolved, a concentration of 148 ppm (0.03/110 × 0.17 × 95.9 × 1000/0.03 = 148 mg/L = 148 ppm) would be formed. Here the Mo concentration of ~100 ppm (Table 2) in the filtrate at the sorption equilibrium is lower than 148 ppm. ICP analysis of the postsorption solid sample (300 ppm Se(VI)) (Table S1) showed 5.5 wt % Mo. EDS analyses also demonstrated the existence of significant amounts of Mo and S (Figure S3) in the solids. All these results support some Mo remained in the solids after sorption. The Mo release into the solution means the sorption is mainly via ion-exchange, while the retained Mo in the postsorption solids indicates the exchange is not complete, reflecting the similar size and charge of MoS₄²⁻ and SeO₄²⁻ in the LDH galleries and their comparable affinity to the LDH layers.

When Hg²⁺ (20 ppm) coexisted with SeO₄²⁻, an increased maximum capacity of ~102 mg/g for Se(VI) was obtained (Table 3). At the V/m value of 1000 mL/g, the ~20 mg/g increased capacity was in agreement with the 20 ppm Hg²⁺ addition. For the pair Se(VI)+Hg, the filtrates after sorption were deep yellow color or colorless depending on the relative ratio of Hg²⁺ to Se(VI) (Figure S4A,B). At trace of Hg²⁺ (0.001–0.4 ppm), deep yellow color was observed, resulting from the released MoS₄²⁻ (Figure S4A). When the concentrations of Hg²⁺ became higher (0.5–50 ppm), the solutions

Table 3. Sorption Data of MoS₄-LDH toward Se(VI)+Hg²⁺ at Different Se(VI) Concentrations and 20 ppm Hg²⁺^a

C ₀ -Hg (ppm)	C ₀ -Se (ppm)	C _f -Se (ppm)	q _e -Se (mg/g)	C _f -Mo (ppm)	pH
20	16.2	0.02	16.2	0.09	3.20 → 4.87
20	104	33.2	70.8	48.1	3.20 → 5.61
20	186	117	69	74.7	3.09 → 5.48
20	273	199	74	68.9	2.94 → 5.35
20	369	275	94	76.8	3.01 → 5.48
20	464	362	102	81.9	3.11 → 5.13

^am = 0.03 g MoS₄-LDH, V = 30 mL, V/m = 1000. Contact time: 24 h.

turned into colorless (Figure S4B), for which an appropriate quantity of Hg²⁺ combined with the MoS₄²⁻ thus preventing the MoS₄²⁻ release into the solution. At a fixed Hg²⁺ concentration of 20 ppm with larger Se(VI) concentrations (20–500 ppm) (Figure S4C), the filtrates displayed much darkened color again, showing the release of MoS₄²⁻ due to the excess of Se(VI) oxoanions. For 10 ppm Se(VI) + 14 ppm Cd²⁺ (Figure S4D), the filtrates were also colorless, similar to the Hg²⁺ case (Figure S4B), suggesting the binding of the metal ions to MoS₄²⁻, preventing its release.

In contrast, for individual Se(IV) oxoanions (without heavy metals present), the sorption reached an equilibrium at around 500 ppm (Table 4), showing a significantly high maximum capacity of ~294 mg/g, displaying the largest value among the reported sorbents (Table 6).^{13–15,48,50,61–71} For comparison, we investigated the sorption of NO₃-LDH as a control experiment (Table S2). We found NO₃-LDH exhibited a much smaller uptake capacity (140 mg/g) for Se(IV). This highlights the key role of the MoS₄²⁻ groups in trapping selenite. In this case, the Mo content in the solution after sorption is ~145 ppm, close to the completely dissolved Mo of 148 ppm we calculated above (0.03 g MoS₄-LDH in 30 mL solution). This means a nearly complete release of Mo into the solution. As shown in Figure S5A, the filtrates after sorptions presented brown color at low concentrations of Se(IV), while colorless at high concentrations, indicating that the released Mo was in the form of MoO₄²⁻. The S²⁻ sites of MoS₄²⁻ may act as the reductant to conduct the reduction of the entered Se(IV). From this phenomenon, we deduce that (1) when Se(IV) oxoanions are in low concentrations, they exchange with

Table 4. Sorption Data of MoS₄-LDH toward Se(IV) at Different Concentrations^a

C ₀ (ppm)	C _f (ppm)	removal (%)	q _e (mg/g)	C-Mo (ppm)	K _d (mL/g)
9.34 ^b	0.080	99.14	9.3	24.1	1.16 × 10 ⁵
20.4 ^c	0.090	99.56	20.3	36.1	2.26 × 10 ⁵
51.1 ^d	0.15	99.71	50.9	66.5	3.40 × 10 ⁵
98.4 ^e	0.15	99.85	98.2	106	6.55 × 10 ⁵
200 ^f	0.090	99.96	200	132	2.22 × 10 ⁶
311 ^g	37.6	87.91	273	145	7.27 × 10 ³
419 ^h	145	65.39	274	145	1.89 × 10 ³
534 ⁱ	240	55.06	294	144	1.23 × 10 ³

^am = 0.03 g, V = 30 mL, V/m = 1000 mL/g. Contact time: 24 h. ^bpH values: 8.57 → 6.29. ^cpH values: 8.31 → 6.34. ^dpH values: 8.29 → 6.04. ^epH values: 8.31 → 7.52. ^fpH values: 8.34 → 8.18. ^gpH values: 8.32 → 9.18. ^hpH values: 8.33 → 9.16. ⁱpH values: 8.34 → 9.52. For the 534 ppm Se(IV), the molar ratio of SeO₃²⁻/MoS₄²⁻ is 4.37, with a much excess. Theoretical saturated Se(IV) concentrations (0.03 g MoS₄-LDH in 30 mL solution) are 122 ppm for SeO₃²⁻ and 244 ppm for HSeO₃⁻.

Table 5. Sorption Data of MoS₄-LDH toward Se(IV)+Cu²⁺ at 20 ppm Cu²⁺ and Varied Se(IV) Concentrations^a

C ₀ -Cu (ppm)	C ₀ -Se (ppm)	C _f -Se (ppm)	q _e -Se (mg/g)	C _f -Mo (ppm)	pH
20	21.1	0.001	21.1	0.34	4.05 → 5.36
20	103	0.03	103	45.3	4.12 → 7.45
20	204	4.64	199	78.2	4.00 → 7.93
20	312	56.9	255	102	4.36 → 8.38
20	420	153	267	116	4.40 → 7.84
20	536	270	267	110	4.52 → 7.96

^am = 0.03 g MoS₄-LDH, V = 30 mL, V/m = 1000. Contact time: 24 h.

Table 6. Comparison of Sorption Capacities of Various Sorbents for Target Elements

elements	sorbents	q _m (mg/g)	ref
Se(IV)	MgAl-MoS ₄ -LDH	294/267	this work
	MgAl-NO ₃ -LDH	140	this work
	MgAl-CO ₃ -LDH ^a	30–90	ref 14
	MgAl-Cl-LDH ^b	119	ref 61
	Mg/Al(Zn/Al)-LDH	119/129	ref 48
	Y ₂ (OH) ₅ Cl·1.5H ₂ O	207	ref 50
	OPBent-2 ^c	5.0	ref 62
	sulfuric-acid-treated peanut shell	43.0	ref 63
	AOCS ^d	1.1	ref 64
	CoFe ₂ O ₄	11.6	ref 65
	CuFe ₂ O ₄	14.1	ref 65
	NU-1000 ^e	102	ref 13
Se(VI)	MgAl-MoS ₄ -LDH	85/102	this work
	NU-1000	62	ref 13
	MgAl-CO ₃ -LDH	30–90	ref 14
	Fe ²⁺ -doped MgAl-LDH ^f	110	ref 15
	Y ₂ (OH) ₅ Cl·1.5H ₂ O	124	ref 50
	CuFe ₂ O ₄ /CoFe ₂ O ₄	5.5	ref 65

^aMgAl layered double hydroxide intercalated by carbonate ions.

^bMgAl layered double hydroxide intercalated by chloride ions.

^cBentonite modification with hexadecylpyridinium and aluminum polyoxy cations. ^dAluminum-oxide-coated sand. ^eZr-Based MOFs.

^fFe²⁺-doped MgAl layered double hydroxide (MgAl-LDH).

MoS₄²⁻ and enter the interlayer space. In this case, the leached MoS₄²⁻ into the solutions causes the reddish color as observed.

(2) when the Se(IV) oxoanions are in excess, some of them react with MoS₄²⁻ in the MoS₄-LDH gallery, and others remaining in the solutions react with the leached MoS₄²⁻, causing the absence of the color.

When 20 ppm Cu²⁺ ions was present (Table 5), a maximum capacity of ~267 mg/g for Se(IV) was observed, with a slightly decreased capacity compare to that of Se(IV) only. Cu²⁺ ions react with the interlayer MoS₄²⁻, which prevents the reduction of Se(IV), thus decreasing the Se(IV) uptake capacity. XRD pattern (Figure S6) of the solid sample after MoS₄-LDH adsorbed 98.8 ppm Cu²⁺ and 122 ppm Se(IV) showed the formation of CuS, verifying the reaction of Cu²⁺ with the S²⁻ of MoS₄²⁻. The less leached Mo amount (110 ppm, Table 5) after saturated sorption, and the colorless solutions after adsorbing 10 ppm Se(IV) + 8 ppm Cu²⁺ (Figure S5B), both proved this point.

The theoretical maximum uptake capacities were calculated based on complete ion exchange (Table S3). For Se(VI), the experimental capacity (84 mg/g) is smaller than the theoretical value (122 mg/g), suggesting incomplete ion-exchange between the SeO₄²⁻ and the starting MoS₄²⁻, due to the comparable affinity of MoS₄²⁻ and SeO₄²⁻ with the LDH layers. For Se(IV), the experimental capacity (294 mg/g) is much larger than the theoretical ones (122/244 mg/g) based on ion-exchange, suggesting that, besides ion-exchange, extra chemical reactions occur.

Langmuir isotherms were normally used to describe the experimental data. For this model, the adsorbate moieties are assumed to undergo monolayer coverage on the surface of the sorbents. This model assumes that once a sorption site is occupied, no further sorption can occur on the same site. The Langmuir isotherm model is shown as eq 1:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (i)$$

where C_e (mg/L) is the concentration at equilibrium, q_e (mg/g) is the equilibrium sorption capacity, q_m (mg/g) is the theoretical maximum sorption capacity, and K_L is the Langmuir constant (L/mg).

Figure 2 displays the equilibrium sorption isotherms. The data points were fitted to the Langmuir model, getting the q_m values of 93, 291, and 101 mg/g for Se(VI), Se(IV), and Se(VI)+Hg²⁺, respectively. The fitted q_m values are close to the corresponding experimental values of 85, 294, and 102 mg/g for Se(VI), Se(IV), and Se(VI)+Hg²⁺, respectively (Tables 2–4), indicating a good fit with the Langmuir isotherms, suggesting a monolayer sorption of them on the surface of MoS₄-LDH. Table S4 also shows the standard deviation for the maximum sorption capacities found from the Langmuir model as well as the values for the Langmuir constant and the correlation coefficient (R^2) for the fitting using the linear equation. The large correlation coefficients show a good fit with the Langmuir isotherm.

Sorption Kinetics Study of Se(IV)/Se(VI) Oxoanions with or without Metal Ions. Sorption kinetics for Se(VI)/Se(IV) oxoanions and mixtures with Hg²⁺/Cu²⁺/Cd²⁺ by MoS₄-LDH was investigated to study the sorption rates and pathways of sorption (Tables 7, 8 and S5–S13). As controls, sorption experiments were also conducted using NO₃-LDH under the same conditions. As shown, for SeO₄²⁻ sorption, Hg²⁺ is very efficient (Table 7), showing extremely rapid removal rates, that is, within 30 min, ≥99% removals and ~10⁵ mL/g K_d

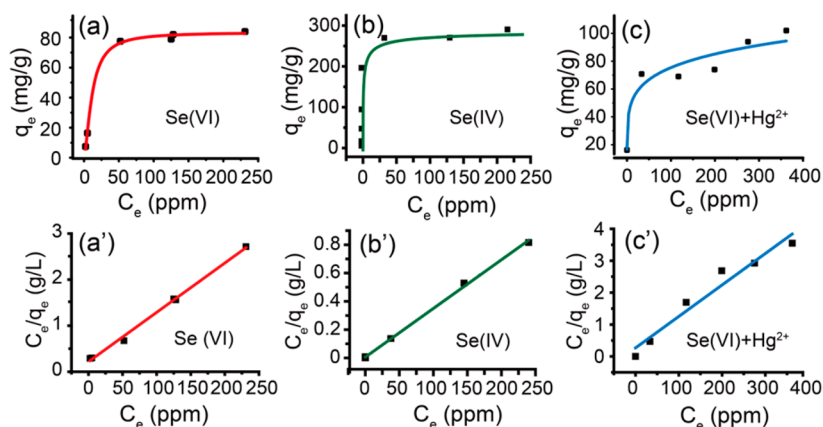


Figure 2. Sorption isotherms for sorption toward oxoanions of Se(IV), Se(VI), and Se(VI)+Hg²⁺ by MoS₄-LDH. Langmuir equilibrium isotherms were derived from equilibrium concentration (C_e , ppm), plotted against q_e (mg/g) and C_e/q_e (g/L).

Table 7. Se(VI)+M²⁺ (M = Hg, Cu) Sorption Kinetics Using MoS₄-LDH and NO₃-LDH^a

		Hg ²⁺ +Se(VI)						
		C ₀ (ppm)	C _f (ppm)					
			1 min	30 min	1 h	4 h	9 h	24 h
MoS ₄ -LDH ^b	Se(VI)	11.0	3.20	0.11	0.11	0.030	0.008	0.008
	Hg ²⁺	23.3	0.107	0.060	0.007	0.001	0.003	0.001
		Hg ²⁺ +Se(VI)						
		C ₀ (ppm)	C _f (ppm)					
			1 min	30 min	1 h	4 h	9 h	24 h
NO ₃ -LDH ^c	Se(VI)	11.00	0.16	0.055	0.048	0.058	0.050	0.050
	Hg ²⁺	23.30	22.60	23.00	22.50	22.30	22.80	17.20
		Cu ²⁺ +Se(VI)						
		C ₀ (ppm)	C _f (ppm)					
			1 min	10 min	30 min	1 h	10 h	24 h
MoS ₄ -LDH ^d	Se(VI)	11.80	8.20	4.50	3.30	3.00	2.10	1.30
	Cu ²⁺	8.13	4.72	1.57	0.042	0.039	0.039	0.020

^a $m = 0.03$ g, $V = 30$ mL, $V/m = 1000$ mL/g. ^bpH values: 2.64 → 4.41. ^cpH values: 2.64 → 4.33. ^dpH values: 4.88 → 5.54.

for both Se(VI) and Hg²⁺ (Table S5). After 9 h, the concentrations of Hg²⁺ and Se(VI) were reduced to 3 and 8 ppb, from 23.3 and 11 ppm, respectively, meeting the required values for drinking water. However, when using NO₃-LDH, the concentrations of Hg²⁺ and Se(IV) were decreased to only 22.8 ppm and 50 ppb from the same starting concentrations, displaying poorer removals than those of MoS₄-LDH. For pair Cu²⁺+Se(VI), as shown in Table 7, Cu²⁺ was not as efficient as Hg²⁺. Even within 24 h, Se(VI) concentration was decreased to only 1.30 ppm (from 11.80 ppm), close to the value without Cu²⁺ present (Table 1).

For selenite sorption, more interestingly, all three metal ions of Hg²⁺, Cu²⁺, and Cd²⁺ are very effective (Tables 8 and S8–S13). As shown, the concentrations of Se(IV) and metal ions were reduced to very low values, for example, 1 ppb Hg²⁺ (from 11.8 ppm) and 9 ppb Se(IV) (from 6.4 ppm) concentrations were obtained within 1 h (Table 8). As a contrast, NO₃-LDH can only give 8.6 ppm Hg²⁺ and 3.3 ppm Se(IV) from the same initial concentrations. In comparison, Hg²⁺ and Cu²⁺ showed much better removals of Se(IV) and Se(VI). Within a contact time of 30 min, the concentrations of Cu²⁺ and Se(IV) can be reduced to 4 and 10 ppb (from their corresponding initial concentrations of 7.8 and 11.3 ppm), far below the permitted value for drinking water. Whereas, when

using NO₃-LDH, Cu²⁺ concentration hardly changed even after 24 h contact time, and Se(IV) concentration was reduced to 0.35 ppm. Cd²⁺ also displayed good synergistic effect for Se(IV) removal. For example, within a contact time of 1 h, Cd²⁺ and Se(IV) can be reduced to 4 and 13 ppb (from the corresponding initial 11.9 and 9.7 ppm), respectively.

Generally, sorption rate is determined by two different rate equations, known as pseudo-first-order and pseudo-second-order mechanisms. Here we employ these mechanisms to describe the sorption behaviors. The comparison was then drawn between the experimental and calculated data. The two kinetic rate equations are as follows.⁶⁶

pseudo-first-order:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{ii})$$

pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{iii})$$

where q_e (mg/g) is the amount of adsorbed element per unit mass of sorbent at equilibrium and q_t (mg/g) is the adsorbed amount at time t , while k_1 (min^{−1}) and k_2 (g/mg min^{−1}) are equilibrium rate constants of pseudo-first-order and pseudo-second-order

Table 8. Se(IV)+M(II) (M = Hg, Cu, Cd) Sorption Kinetics Using MoS₄-LDH and NO₃-LDH^a

		Se(IV)+Hg ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			10 min	30 min	1 h	9 h	11 h	24 h
MoS ₄ -LDH ^b	Hg ²⁺	11.8	0.009	0.007	0.001	<0.001	<0.001	0.001
	Se(IV)	6.4	5.26	1.32	0.009	<0.001	<0.001	<0.001
		Se(IV)+Hg ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			30 min	1 h	4 h	9 h	11 h	24 h
NO ₃ -LDH ^c	Hg ²⁺	11.8	11.4	8.6	9.2	4.5	4.0	3.1
	Se(IV)	6.4	4.5	3.3	3.0	2.1	2.1	1.7
		Se(IV)+Cu ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			1 min	10 min	30 min	1 h	7 h	10 h
MoS ₄ -LDH ^d	Cu ²⁺	7.81	1.30	0.033	0.004	0.009	0.012	0.010
	Se(IV)	11.3	4.54	0.010	0.010	0.030	0.030	0.030
		Se(IV)+Cu ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			1 min	10 min	30 min	1 h	7 h	10 h
NO ₃ -LDH ^e	Cu ²⁺	7.95	7.94	7.94	7.94	7.93	7.92	7.93
	Se(IV)	12.5	0.46	0.35	0.26	0.27	0.26	0.35
		Se(IV) + Cd ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			1 min	10 min	30 min	1 h	4 h	7 h
MoS ₄ -LDH ^f	Cd ²⁺	11.9	8.92	2.34	0.052	0.004	0.001	0.001
	Se(IV)	9.66	4.76	0.025	0.020	0.013	0.014	0.009
		Se(IV) + Cd ²⁺						
		C ₀ (ppm)	C _f (ppm)					
			1 min	10 min	30 min	1 h	4 h	7 h
NO ₃ -LDH ^g	Cd ²⁺	11.9	11.8	11.8	11.7	11.7	11.8	11.8
	Se(IV)	9.66	0.35	0.33	0.24	0.15	0.17	0.20

^am = 0.03 g, V = 30 mL, V/m = 1000 mL/g. ^bpH values: 2.64 → 4.41. ^cpH values: 2.64 → 4.33. ^dpH values: 4.88 → 5.54. ^epH values: 5.82 → 4.62. ^fpH values: 4.76 → 5.60. ^gpH values: 4.76 → 5.72.

sorption interactions, respectively. The k_1 value was obtained by plotting $\ln(q_e - q_t)$ against t and k_2 by plotting t/q_t against t .

Sorption kinetics curves for Se(VI)/Se(IV)+M (M = Hg²⁺, Cu²⁺ and Cd²⁺) by MoS₄-LDH and NO₃-LDH are shown in Figures 3, 4, S7, and S8. The linear relationship of t/q_t versus t gives the kinetic parameters shown in Table S14. The calculated sorption capacities ($q_{e,cal}$) from the pseudo-second-order model are much closer to experimental values ($q_{e,exp}$), and the goodness of fit coefficients (R^2) are ~1, indicating the sorption for these elements by the MoS₄-LDH and NO₃-LDH can be well-described with a pseudo-second-order kinetic model, consistent with a chemisorption process.⁶⁷ The different k_2 values reflect the different effect of the metal ions on the Se(VI) and Se(IV) capture (Table S14).

Selective Uptake toward Mixtures of Oxoanions of As(III)/As(V)/Cr(VI)/Se(VI)/Se(IV) and Metal Ions of Hg²⁺/Cd²⁺/Cu²⁺. From Table S15–S17, we can see that when all of the oxoanions and metal ions were put together, the concentrations of Se and metal ions were reduced to <1 ppb (from 1000 to 2000 ppb), well matching the requirement of drinking water. However, for As(III)/As(V)/Cr(VI) oxoanions, none of them can be reduced to a ppb level concentration, even giving worse results in comparison to those without the metal

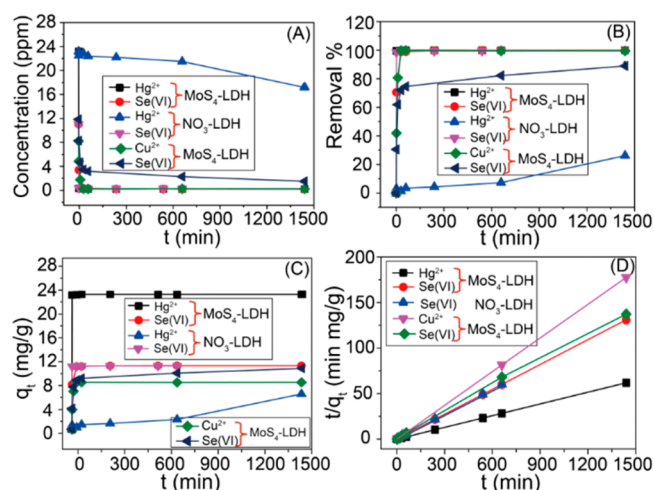


Figure 3. Sorption kinetics curves for Se(VI)+M (M = Hg²⁺, Cu²⁺) by MoS₄-LDH and NO₃-LDH: (a) Concentration change with contact time, (b) removal % as a function of contact time, (c) sorption capacity (q_t) with contact time, and (d) pseudo-second-order kinetic plots.

ions present.⁵⁶ This highlights the wonderful promotive effect of the metal ions for the selenium capture but not others.

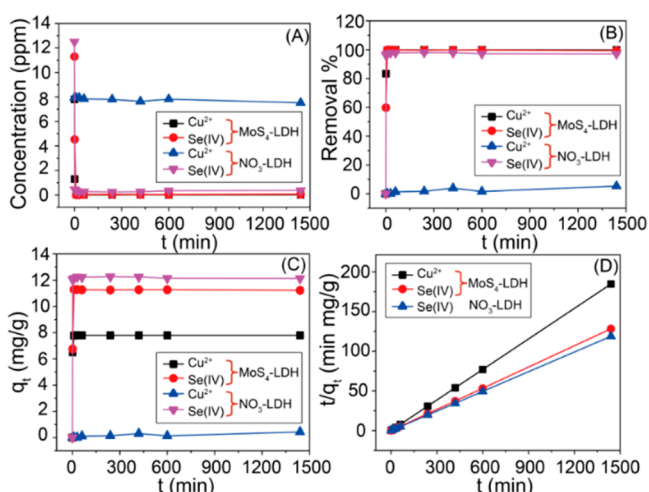


Figure 4. Sorption kinetics curves for Se(IV)+Cu²⁺ by MoS₄-LDH and NO₃-LDH: (a) Concentration change following contact time, (b) removal % as a function of contact time, (c) sorption capacity (q_t) with contact time, and (d) pseudo-second-order kinetic plots for the sorption.

Structure and Morphology Characterization of the Solid Samples after Sorption. After the sorption experiments, the solid samples were air-dried and analyzed by XRD, IR, and SEM observations. From the SEM observations (Figure 5), after adsorbing individual oxoanions and mixtures with metal ions, the samples fully maintained the hexagonal prismatic shape, confirming the dominant layered phases after the sorption process.

At a low concentration of Se(VI) (10 ppm), the sample after sorption exhibited a d_{basal} value of 1.07 nm (Figure 1A-b), close to that of the MoS₄-LDH precursor (Figure 1A-a). At this moment the adsorbed Se(VI) amount is not large enough to produce a new discernible phase, thus the MoS₄-LDH phase would act as the dominant phase. At a higher concentration of 50 ppm (Figure 1A-c), a 0.92 nm d_{basal} became more discernible besides the 1.06 nm. At > 50 ppm Se(VI), a single phase of 0.93 nm d_{basal} was observed (Figure 1A-d,e). In order to compare the d_{basal} values of the completely intercalated products of the Se-oxoanions, we prepared LDH samples specifically intercalated with these anions. XRD patterns of these control samples are shown in Figure S9A. The as-prepared products showed d_{basal} values of 0.94/0.96 nm for SeO₃-LDH (Figure S9A-c,d) and 0.92 nm for SeO₄-LDH (Figure S9A-e), in agreement with reference values.^{61,68} From Figure 1A-e, we see the fully loaded sample of SeO₄²⁻ exhibited a d_{basal} (0.93 nm), close to the d_{basal} of SeO₄-LDH (0.92 nm) we prepared, suggesting a LDH intercalated phase mainly by SeO₄²⁻. But the large amount of Mo and S by EDS (Figure S3) and ICP analyses of the fully loaded sample (Table S1) revealed the existence of MoS₄²⁻. However, the Se/Mo molar ratio of ~1.9 suggests an excess of the SeO₄²⁻ intercalated phase, coincident with the d_{basal} of 0.93 nm assigned to SeO₄-LDH.

For the Se(IV) adsorbed samples, lower Se(IV) concentration (20 ppm) generated a d_{basal} value of 1.05 nm (Figure 6A-a), close to the that of MoS₄-LDH precursor (Figure 1a). At a higher Se(IV) concentration of 50 ppm (Figure 6A-b), a 0.93 nm d_{basal} became more discernible, because of the

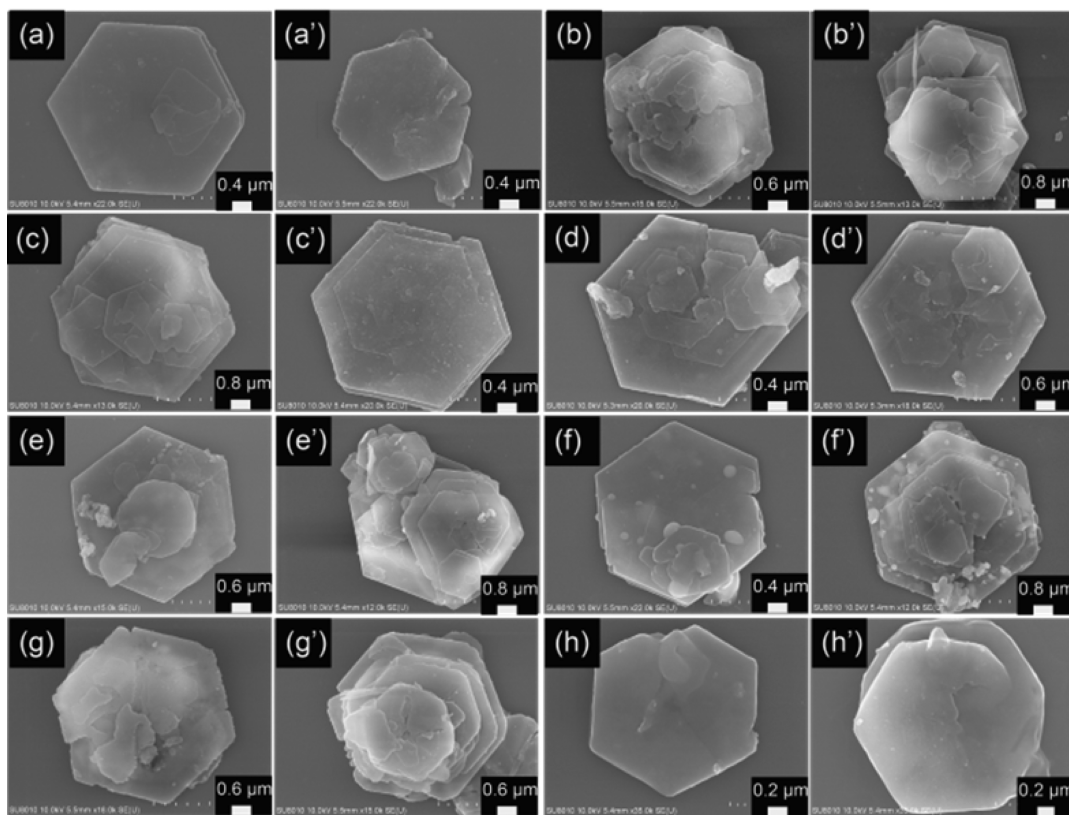


Figure 5. SEM images of the samples after MoS₄-LDH adsorbed of (a, a') 10 ppm Se(VI), (b, b') 300 ppm Se(VI), (c, c') 464 ppm Se(VI)+20 ppm Hg²⁺, (d, d') 136 ppm Se(VI)+360 ppm Hg²⁺, (e, e') 20 ppm Se(IV), (f, f') 400 ppm Se(IV), (g, g') 20 ppm Se(IV)+20 ppm Cu²⁺, and (h, h') 400 ppm Se(IV)+20 ppm Cu²⁺.

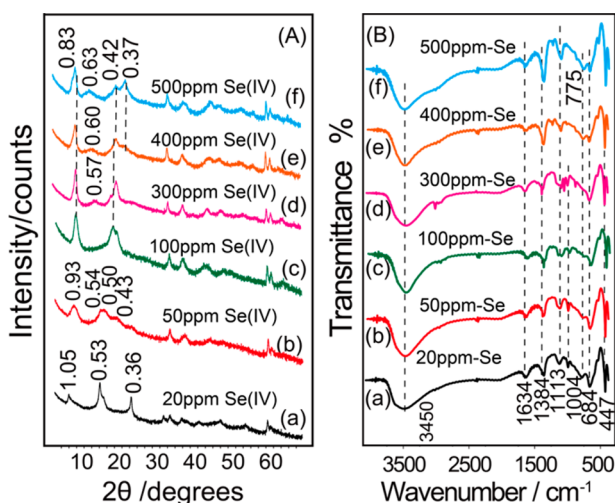


Figure 6. (A) XRD patterns and (B) IR spectra of samples after $\text{MoS}_4\text{-LDH}$ adsorbed Se(IV) at different concentrations.

decreased $\text{MoS}_4\text{-LDH}$ phase and intercalation with other anions. At Se(IV) concentrations of >100 ppm (Figure 6A-c-f), a 0.83 nm d_{basal} became prominent, accompanied a new peak at 0.63 nm, in agreement with previous report on this compound.⁶¹ Considering the d_{basal} of 0.96 nm for $\text{SeO}_3\text{-LDH}$, the 0.83 nm d_{basal} should not be from the SeO_3^{2-} intercalation. Moreover, as discussed above, nearly all Mo was leached into the solution (145 ppm, Table 4) in the fully loaded sample, so the interlayer anions should not be Mo-involving anions. As shown in the XPS data, the Se $3d_{5/2}$ energy of Se(IV) in Na_2SeO_3 was 58.0 eV (Figure 7a), while in the adsorbed samples, the Se $3d_{5/2}$

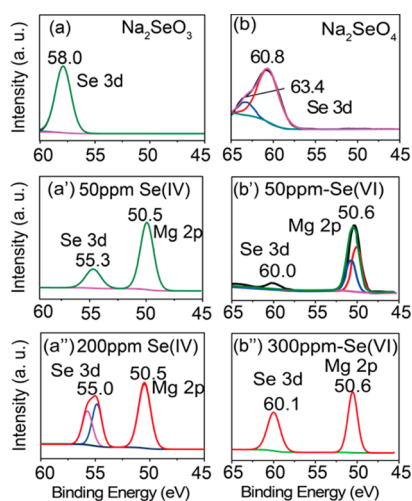


Figure 7. XPS showing Se $3d$ peaks of (a) Na_2SeO_3 precursor and after $\text{MoS}_4\text{-LDH}$ adsorbed (a') 50 ppm and (a'') 200 ppm Se(IV) ; (b) Na_2SeO_4 precursor and after $\text{MoS}_4\text{-LDH}$ adsorbed (b') 50 ppm and (b'') 300 ppm Se(VI) .

energies were ~ 55 eV, showing the Se(IV) was reduced to Se(0) .⁶⁹ This demonstrates that Se(IV) was reduced during the sorption process, explaining the absence of $\text{SeO}_3^{2-}/\text{HSeO}_3^-$ in postsorption samples. Since the interlayer MoS_4^{2-} anions were absent (being exchanged or reacted), what are the newly entered counter-anions in the final LDH materials? From reference, we know the 0.83 nm d_{basal} is close to that of the LDH intercalated by SO_4^{2-} ,⁵² and thus the SO_4^{2-} , arising from

the oxidation of S^{2-} ions released from MoS_4^{2-} (the oxidizing agents are Se(IV) and O_2 in air), would be the most probable anions. The XPS peaks at $168\text{--}170$ eV (Figure S10) support the presence of SO_4^{2-} . The IR band at 1113 cm^{-1} (Figure 6B) is also assigned to SO_4^{2-} ,⁵² further verifying the existence of SO_4^{2-} . In our previous work, we also found the gallery S_x^{2-} ions in LDH gallery were oxidized to form $\text{SO}_4\text{-LDH}$ during the sorption Hg^0 vapor using $\text{S}_x\text{-LDH}$.⁵²

The metal ions play an interesting role in the capture of Se(VI) and Se(IV) . XRD patterns of the solid samples after $\text{MoS}_4\text{-LDH}$ adsorbed Se(VI)+Hg^{2+} at different concentrations (Figure 8A) can give us some exhibitions. Lower

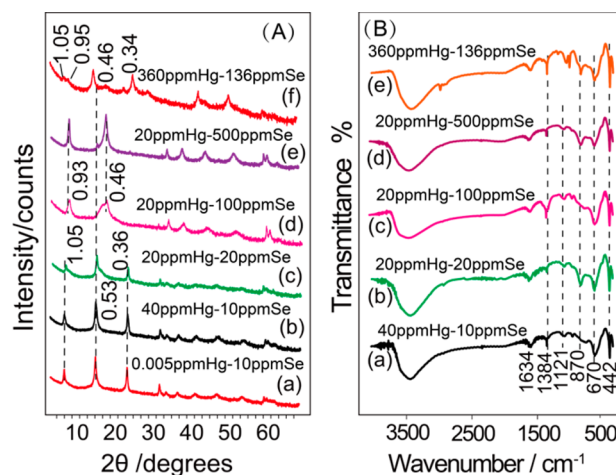


Figure 8. (A) XRD patterns and (B) IR spectra of the samples after $\text{MoS}_4\text{-LDH}$ adsorbed Se(VI)+Hg^{2+} at different concentrations.

concentrations of Hg^{2+} ($0.005\text{--}40$ ppm) and Se(IV) (10 and 20 ppm) did not change the d_{basal} (1.05 nm, Figure 8A-a-c), suggesting $\text{MoS}_4\text{-LDH}$ as a dominant phase. Keeping Hg^{2+} concentration constant at 20 ppm and the Se(VI) concentrations varied in the range of $100\text{--}500$ ppm, a d_{basal} of 0.93 nm (Figure 8A-d,e) was observed, meaning a dominant SeO_4^{2-} intercalated LDH. A combination of 360 ppm Hg^{2+} and 136 ppm Se(VI) sample revealed two d_{basal} of 1.05 and 0.95 nm (Figure 8A-f), indicating the concurrent existence of $\text{MoS}_4\text{-LDH}$ and $\text{SeO}_4\text{-LDH}$. A very slow scan rate of XRD data collection (Figure S11) (with step size of 0.00167° , scan time of 100 s per step) revealed the presence of HgS , which means some of the MoS_4^{2-} ions degraded during the sorption process. A control experiment with 200 ppm Se(VI) alone did not show the presence of HgS (Figure S11). Thus, we conclude that during the sorption of Hg^{2+} , the interlayer MoS_4^{2-} may react with Hg^{2+} to form HgMoS_4 first and then decompose to HgS . The sorption process is very complex, including the formation of HgS and mixed intercalation phases involving the starting MoS_4^{2-} and newly entered SeO_4^{2-} .

For pairs of Se(IV)+M (for example, $\text{M} = \text{Cu}^{2+}$), low concentrations of metal ions did not result in a change of the d_{basal} (Figure 9A-b). At much higher concentrations of Cu^{2+} and Se(IV) , decreased d_{basal} values ($0.86\text{--}0.93$ nm, Figure 9A-c-f) became distinct, indicating possible formation of NO_3^- intercalated phase. In IR spectroscopy data of the 98.8 ppm Cu^{2+} and 122 ppm Se(IV) postsorption sample (Figure 9B-f), the 1384 cm^{-1} for NO_3^- band was observable. This signifies that during the capture of Se(IV) along with the metal nitrates, the metal ions and selenites both reacted with MoS_4^{2-} , and for

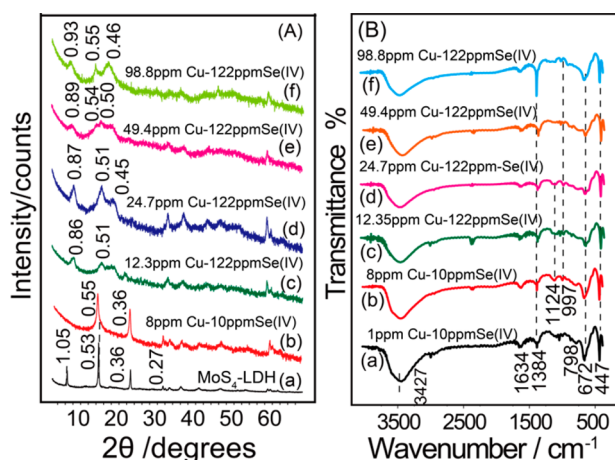


Figure 9. (A) XRD patterns and (B) IR spectra of the samples after MoS₄-LDH adsorbed Se(IV)+Cu²⁺ at different concentrations.

making up the negative charge, NO₃[−] anions entered into the interlayers. From the XRD patterns of samples at slow scan rates, CuS (or HgS for Hg²⁺ case) was distinctly observed (Figure S6). This is similar to that observed for the Se(VI)+M cases, indicating the MS salts were preferably formed during sorption.

IR spectra of the loaded solid samples confirmed the capture of the oxoanions and the stability of the LDH materials after sorption. For SeO₄^{2−} with and without metal ions (Figures 1B and 8B), the bands at 877/870 cm^{−1} were assigned to ν (Se–O) vibrations, as found in the SeO₄-LDH precursor and the salts of Na₂SeO₄, in good agreement with the reference values.^{14,70,71}

For the Se(VI) adsorbed samples (such as 50 and 300 ppm concentrations), the Se 3d energy at ~60 eV for Se(VI) (Figure 7b',b'') is in agreement with the 60.8 eV of the Na₂SeO₄ precursor (Figure 7b). For 20 ppm Hg+500 ppm Se(VI) sample (Figure 10a'), Se 3d energy was 59.8 eV. All these data demonstrate the valence of Se(VI) does not change during sorption for Se(VI) with and without metal ions. The peaks at 104.7 and 100.7 eV (Figure 10a) assigned to Hg 4f_{5/2} and 4f_{7/2} energies of Hg²⁺.^{72,73}

For individual Se(IV), as discussed above, the XPS data showed Se(IV) was reduced to Se⁰ during sorption (Figure 7a–a''). For Se(IV)+M, the 54–55 eV energies assigned to Se 3d of Se⁰ showed similar reduction of Se(IV).⁶⁹ However, the reduction from Se(IV) to Se⁰ may be not mainly companied with the oxidation of S^{2−} to SO₄^{2−}, since the peaks of S 2p energy (~168 eV) for SO₄^{2−} were weak (Figure S12), thus the S^{2−} may be possibly oxidized to S₈ as found in our previous work when the S_x-LDH adsorbed I₂ vapor.⁵⁴

For the pair 14.2 ppm Cd(II)+10 ppm Se(IV), Cd 3d energies of 404.7 and 411.4 eV (Figure 10b) indicate the uptake of Cd²⁺. For 25.4 ppm Hg(II)+10 ppm Se(IV), the peaks at 103.7 and 99.7 eV (Figure 10c) were assigned to Hg 4f_{5/2} and 4f_{7/2} energies of Hg²⁺,^{72,73} respectively, demonstrating the capture of Hg²⁺. For 20 ppm Cu(II)+20 ppm Se(IV) and 98.8 ppm Cu(II)+120 ppm Se(IV), the energies of 953.2/952.3 and 933.4/932.5 eV are assigned to Cu 2p_{1/2} and Cu 2p_{3/2} (Figure 10d, e). In addition, the Se 3p energies around 163 eV (Se 3p_{1/2}) and 170 eV (Se 3p_{3/2}) also verified the capture of selenium (Figures S10 and S12). The Mo 3d energies (Figures S1, S10, and S12) in the adsorbed samples showed very close values (~232 and ~229 eV ascribed to Mo 3d_{5/2}

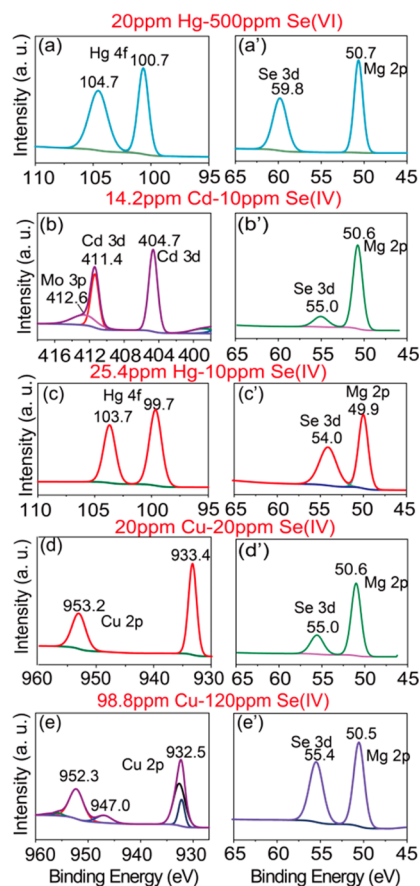


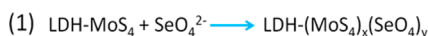
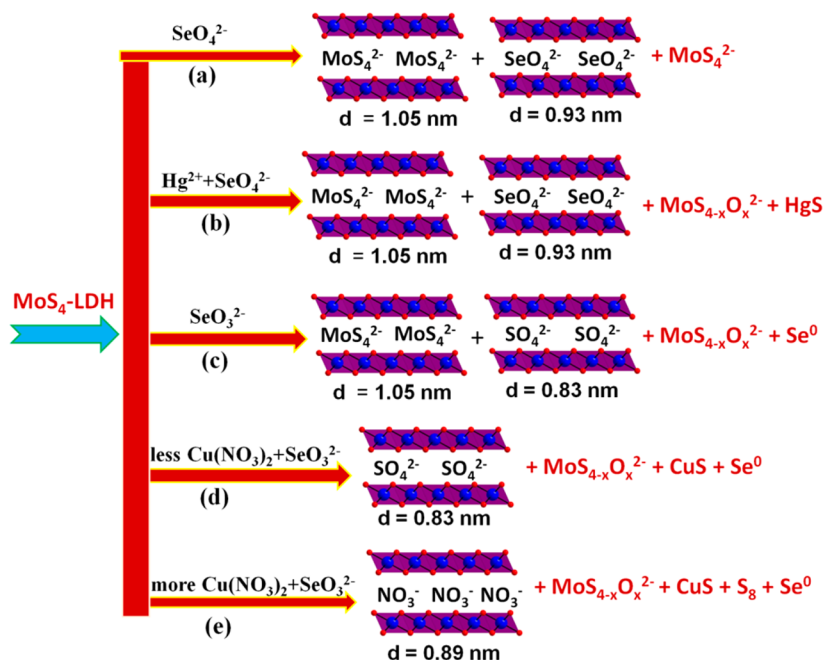
Figure 10. XPS showing the MoS₄-LDH adsorbed samples: (a) Hg 4f and (a') Se 3d peaks for 20 ppm Hg+500 ppm Se(VI), (b) Cd 3d and (b') Se 3d peaks for 14.2 ppm Cd+10 ppm Se(IV), (c) Hg 4f and (c') Se 3d peaks for 25.4 ppm Hg+10 ppm Se(IV), (d) Cu 2p and (d') Se 3d peaks for 20 ppm Cu+20 ppm Se(IV), (e) Cu 2p and (e') Se 3d peaks for 98.8 ppm Cu+120 ppm Se(IV).

and Mo 3d_{5/2} energies of Mo(VI)) to those of the MoS₄-LDH precursor (Figure S1b), suggesting the oxidation state of Mo(VI) did not change during the sorption.

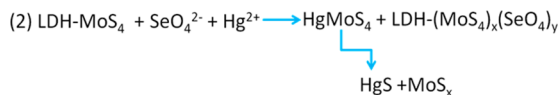
Sorption Mechanism for Se(IV)/Se(VI) Oxoanions with or without Metal Ions. As discussed above, the capture of the individual Se(IV)/Se(VI) oxoanions can proceed by anion exchange, and/or chemical reactions of the oxoanions with the interlayer MoS₄^{2−}. During the sorption of SeO₄^{2−}, Na⁺ concentrations before and after the sorptions were found to be nearly consistent. This suggests anion exchange is a dominating path. However, because of the high affinity of MoS₄^{2−} to the LDH layers, the exchange reactions were not complete. For Se(VI)+M, the metal ions can react with the MoS₄^{2−}, thus increasing the entrance of SeO₄^{2−}. For individual Se(IV), the reduction of Se(IV) to Se(0) occurred, and SO₄^{2−} resulting from the oxidation of S^{2−} of MoS₄^{2−} acted as the interlayer anions to substitute the MoS₄^{2−} (Mo became MoO₄^{2−} and went into solutions). The addition of metal ions can increase the removal rate for Se(IV) but decrease the uptake capacity.

We thus conceive the sorption mechanism of MoS₄-LDH toward Se(IV)/Se(VI) oxoanions and metal ions as follows:

(1) During adsorbing individual SeO₄^{2−}, mixture phases of LDH-(MoS₄^{2−})_x(SeO₄^{2−})_y would be formed, whose d_{basal} values depended on the quantity of each phase with either MoS₄^{2−} or SeO₄^{2−} (see formula 1, Scheme 1a).

Scheme 1. Possible Sorption Mechanisms during MoS₄-LDH Adsorbed SeO₄²⁻ and SeO₃²⁻ with and without Metal Ions

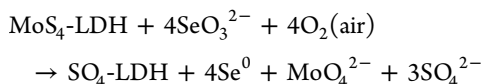
(2) For $\text{SeO}_4^{2-} + \text{M}$ ($\text{M} = \text{Hg}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}$), besides the formation of the mixture phases $\text{LDH-(MoS}_4)_x(\text{SeO}_4)_y$, the metal ions will react with the MoS_4^{2-} to form MS (see formula 2, Scheme 1b). At this moment, the reaction of the metal ions and MoS_4^{2-} and the precipitation of metal sulfides improve the sorption toward the SeO_4^{2-} .



(3) For individual SeO_3^{2-} , the anions react with MoS_4^{2-} in the solid sorbent and also in solutions. In the solid sorbent, the $\text{LDH-(MoS}_4)_x(\text{SO}_4)_y$ phases may form (see Scheme 1c). At higher Se(IV) concentrations, $\text{SO}_4\text{-LDH}$ phase ($d = 0.83 \text{ nm}$) will be distinct. During the processes, oxidation–reduction reactions between Se(IV) and S^{2-} produce Se^0 and air oxidation of sulfide ions forms SO_4^{2-} ions which maintain the interlayer, and Mo leaches into the solution as $\text{MoS}_{4-x}\text{O}_x^{2-}$ forms (formula 3, Scheme 1c).

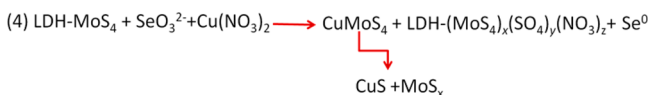


When sufficient SeO_3^{2-} ions are present, the proper reaction is



(4) For $\text{SeO}_3^{2-} + \text{M}$ ($\text{M} = \text{Hg}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}$), besides the formation of mixture phases of $\text{LDH-(MoS}_4)_x(\text{SO}_4)_y(\text{NO}_3)_z$, the metal ions react with the MoS_4^{2-} to form MS (formula 4, Scheme 1d,e). The interlayer anions would be MoS_4^{2-} , SO_4^{2-} (when $\text{M}(\text{NO}_3)_2$ salts are less), or NO_3^- (when $\text{M}(\text{NO}_3)_2$ salts are in excess). At this time, the Mo may leach into the solution as $\text{MoS}_{4-x}\text{O}_x^{2-}$ anions.

Here, the common characteristic for both Se(VI)+M and Se(IV)+M is the formation of MS salts but not MSe.



CONCLUDING REMARKS

The Se(VI)/Se(IV) oxoanions are difficult species to remove from complex solutions. The MoS₄-LDH material demonstrates excellent performance for fast and highly efficient simultaneous removal of the toxic Se(VI)/Se(IV) oxoanions as well as quantitative removal of heavy metals (Hg^{2+} , Cu^{2+} , and Cd^{2+}). Within a period of several minutes, the concentrations of Se(IV)/Se(VI) and metal ions can be simultaneously reduced to very low values (ppb level) which are well below those required for drinking water. The MoS₄-LDH exhibits an enormous sorption capacity of 294 mg/g for Se(IV), reaching a record value among the top previously reported materials (Table 6). The extremely fast capture and high capacity for selenite would be ascribed to the reduction of Se(IV) to Se⁰ by the S²⁻ sites in MoS₄²⁻ of the MoS₄-LDH. For $\text{SeO}_4^{2-} + \text{M}$, the high removal capability may be attributed to the reactions of the entered metal ions with the interlayer MoS₄²⁻, giving the chance to SeO_4^{2-} to enter the interlayer space. These results make the MoS₄-LDH material a compelling candidate for the application in remediation of water polluted with selenium oxoanions and heavy metal ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b07123.

Elemental contents in the postsorption samples by MoS₄-LDH, sorption data of NO₃-LDH toward Se(IV), experimental and calculated values of maximum uptake capacities for oxoanions, kinetics data of sorptions of Hg+Se(VI), Cu+Se(VI), Cu+Se(IV), Hg+Se(IV), and Cd

+Se(IV) using MoS₄-LDH and NO₃-LDH, kinetic parameters for adsorbing Se(VI)/Se(IV)+M²⁺, removals of MoS₄-LDH for mixtures of Hg(II)+Cu(II)+Cd(II)+Se(VI)+As(V)+Cr(VI), Hg(II)+Cu(II)+Cd(II)+Se(IV)+Se(VI)+As(III)+As(IV)+Cr(VI), Hg(II)+Cu(II)+Cd(II)+Se(IV)+As(III), XPS of (NH₄)₂MoS₄, MoS₄-LDH, and postsorption samples, photographs and UV–visible spectroscopy of supernatants after MoS₄-LDH adsorbed SeO₄²⁻, EDS and chemical composition of Se(VI) postsorption samples by MoS₄-LDH, photographs of supernatants after MoS₄-LDH adsorbed Se(VI)+M²⁺, Se(IV), and Se(IV)+Cu²⁺, XRD patterns (at slow scan rates) of samples after MoS₄-LDH adsorbed Cu²⁺+Se(IV) and Hg²⁺+Se(IV), Hg+Se(VI), and Se(VI), sorption kinetics for Se(IV)+Hg²⁺ and Se(IV)+Cd²⁺ by MoS₄-LDH and NO₃-LDH, XRD patterns and IR spectra of NO₃-LDH and Ha₂SeO₃ and samples after NO₃-LDH was ion-exchanged with SeO₃²⁻ and SeO₄²⁻, XPS spectra after MoS₄-LDH adsorbed Hg+Se(VI), Cd+Se(IV), Hg+Se(IV), and Cu+Se(IV), and Se(IV) (PDF)

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Notes

The authors declare no competing financial interest.

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