

Supplementary Material

Selenium Oxoanions Removal from Wastewater by MoS_4^{2-} -Intercalated FeMgAl LDH: Catalytic Roles of Fe and Mechanism Insights

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1 Supplementary Data

S1. Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and hex-methylene tetra-amine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$, AR, 99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium hydroxide (96%) and ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$) were purchased by J&K Chemical Ltd. (Shanghai, China), sodium selenite (NaSeO_3 , AR, 99.9%) and sodium selenate decahydrate ($\text{NaSeO}_4 \cdot 10\text{H}_2\text{O}$, AR, 99.9%) were purchased from Alfa Aesar. Deionized water (18.0 mΩ cm) was collected by a Millipore Milli-Q system (USA), boiled and bubbled with nitrogen for 15 minutes and applied through all of the experiments. All reagents applied in experiments were of analytical reagent grade and used as received without any further purification.

S2. Synthesis routes of FeMgAl- CO_3 , FeMgAl- NO_3 , FeMgAl- MoS_4 , MgAl- CO_3 , MgAl- NO_3 , and MgAl- MoS_4

FeMgAl- CO_3 : For FeMgAl- CO_3 preparation, proper amount materials, as 0.3 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.5 mM), 2.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (12.5 mM), 1.2 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (5 mM) were mixed in 50 ml deionized water, adding with 2.5 g HMT (17.5 mM), all mixed and use Teflon-lined autoclave for these mixture hydrothermal process, for 24 h under the temperature of 140 °C, after cool down through running cold water, followed with vacuum filtration, and washed with degassed deionized water for three times, and resultant muddy materials were dried in 60 °C under vacuum drier for 24 h.

FeMgAl- NO_3 : FeMgAl- NO_3 was obtained through the ion-exchange process, as 102.0 g NaNO_3 dissolved into 300 mL deionized water, 0.8 g FeMgAl- CO_3 put into water, nitrogen was purged into the system with the speed of 0.05L/min through sealed conical flask, to avoid, or at least minimize the pollution of CO_2 from the

air. The mixture stirred under room temperature (25 °C) for 24h, followed with vacuum filtration and dried in 60 °C under vacuum situation.

FeMgAl-MoS₄: FeMgAl-MoS₄ LDH synthesized by simultaneously adding 0.5 g FeMgAl-NO₃ LDH and 0.5 g (NH₄)₂MoS₄ into 25 mL deionized water, ultra-sonication for 10 min and stirring for 24 h under room temperature (25 °C), all the stirring processes were purged into system with the speed of 0.05 L/min through sealed conical flask, also to avoid the pollution of CO₂ from the air. Resultant solid phase was washed and vacuum filtrated, dried under 40 °C in a vacuum drying oven for 24 h.

MgAl-CO₃, MgAl-NO₃, and MgAl-MoS₄: these three adsorbents also prepared for control experiments and disclosure reactions mechanisms. CO₃²⁻ intercalated Mg/Al layered double hydroxide (MgAl-CO₃ LDH, abbr. MgAl-CO₃) was synthesized through one-pot method, and without adding of iron ions, 14 mM MgCl₂·6H₂O and 5 mM AlCl₃·6H₂O to form the molar ratio of Mg²⁺: Al³⁺ is 14:5, other reaction processes are same with preparation of FeMgAl LDHs. After that, NO₃⁻ intercalated Mg/Al layered double hydroxide (MgAl-NO₃ LDH, abbr. MgAl-NO₃), and MgAl-MoS₄ LDH was synthesized with two-step ion-exchange experiments, which are same with FeMgAl-MoS₄ preparation.

S3. Characterization

Physical characterization and chemical analysis of different adsorbents were demonstrated through various methods. The elemental analysis (content of C, S, and N) was conducted by elemental analyzer Vario Micro cube Elementary (German), functional groups detected by Fourier transform infrared spectrometer (FT-IR) spectra through KBr pellet method, over the wavelength range from 4000 ~ 400 cm⁻¹ by Vertex 70 (USA). Crystal structure of different adsorbents before and after sorption reactions was measured by X'Pert PRO X-ray photoelectron spectrometer (PANalytical B.V, Holland) for X-ray diffraction spectra (XRD), with Cu K α radiation (λ =0.1542 nm) over a 2 θ collection range of 5~80° with a scanning rate of 2°/min-1. Detailed surface and shape information of adsorbents were obtained through a scanning electron microscope (SEM), conducted by Quanta 200 ESEM (FET, Holland) cooperated with an electron dispersive X-ray (EDX). The components of FeMgAl-MoS₄, as well as selenium and other species concentrations, were measured by inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC-e, PerkinElmer, USA), content of metal ions in LDHs were detected by ICP-MS, after digestion of 0.01 g adsorbents in a HNO₃:H₂O₂:HClO₄ mixed solution (2:2:1) with total volume is 25 mL for 24 h. X-ray photoelectron spectroscopy(XPS) information obtained from AXIS-ULTRA DLD-600W (Kratos, Japan), using an X-peaks fitting of the peaks.

S4. Quantitative Study

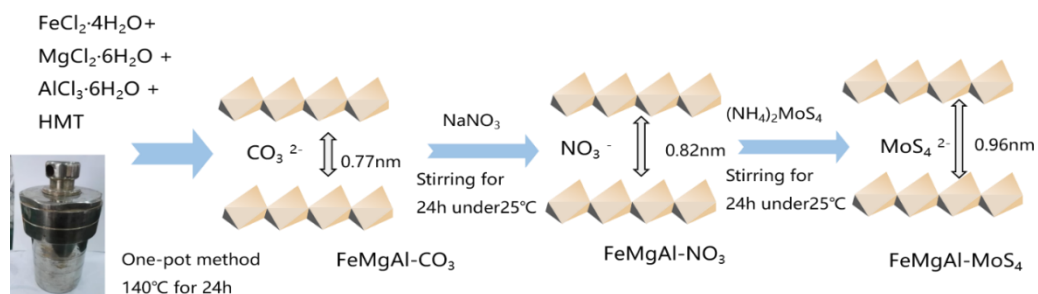
For comparison of directly reduced selenium amount with the heterogeneous FeMgAl-MoS₄ reduced amount, homogeneous experiments conducted by adding 4.3 mg (NH₄)₂MoS₄ for 10 mL solutions, in order to simulate the same amount of MoS₄²⁻ groups in FeMgAl-MoS₄. For the same reason, the proper amount of iron ions, 0.9 mg FeCl₂·4H₂O and 3.42 mg FeCl₃·6H₂O to simulate the Fe content and molar ratio of FeMgAl-MoS₄ for each 10 mL solutions, 1000 ppm Se (IV) or Se (VI) was used to evaluate maximum adsorptive capacities. Moreover, without Fe experiments conducted with only (NH₄)₂MoS₄, MgAl-NO₃, and MgAl-MoS₄, and homogeneous Fe experiments conducted by using FeCl₂·4H₂O and FeCl₃·6H₂O as Fe sources instead of Fe-contained LDHs. FeMgAl-NO₃ and FeMgAl-MoS₄ were regarded as heterogeneous Fe sources and used for heterogeneous experiments. XPS also involved to computable experiments with the aim of elucidation of reaction mechanisms.

The maximum capacities of Fe-MoS₄ adsorbents toward the selenium the oxoanions of Se(IV) and Se(VI) were conducted by adding 0.01 g of Fe-MoS₄ adsorbents into 10 mL aqueous solutions in 30 mL

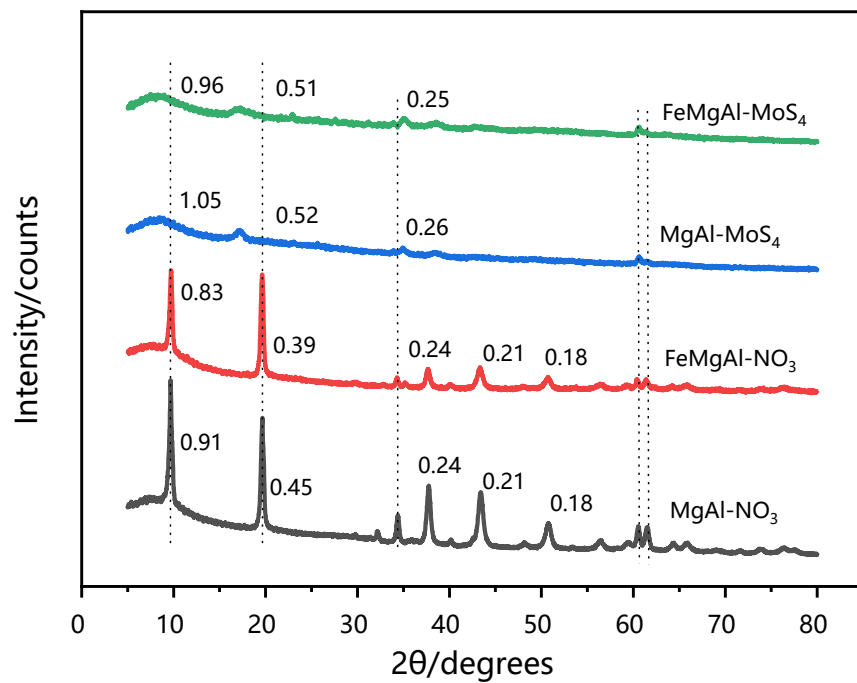
polypropylene centrifuge tubes for different selenium concentrations (10-1000 ppm), being shaken for 24 h under 25 °C in an oscillator to reach equilibrium, the solid and solution were separated through centrifugation after adsorption. Sorption kinetics of FeMgAl-MoS₄ conducted at different time intervals from 5 min to 24 h. 0.01 g FeMgAl-MoS₄ was added into 10 mL (m/V=1.0 g/L) solutions for each operation. After specific time intervals, suspensions were centrifuged and supernatants were conducted for ICP-MS analysis.

2 Supplementary Figures and Tables

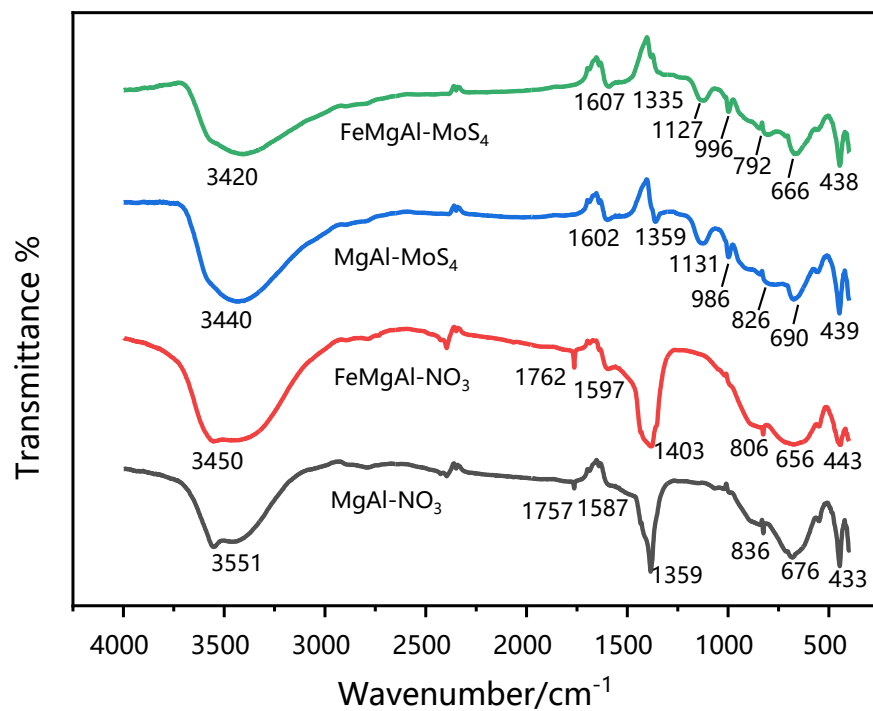
2.1. Supplementary Figures



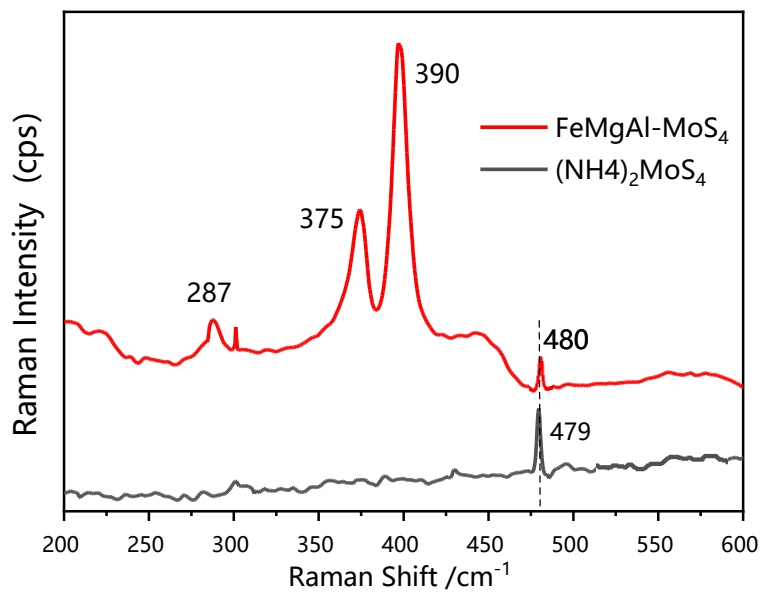
Supplementary Figure S1. Scheme of adsorbents preparation.



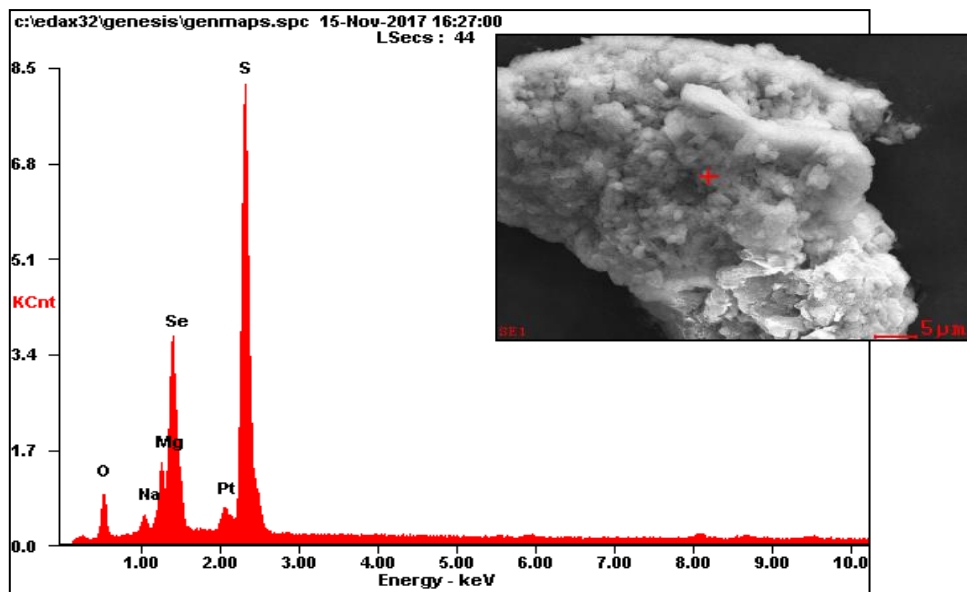
Supplementary Figure S2. XRD patterns of FeMgAl-MoS₄, MgAl-MoS₄, MgAl-NO₃ and FeMgAl-NO₃.



Supplementary Figure S3. FT-IR spectra of FeMgAl-MoS₄, MgAl-MoS₄, MgAl-NO₃ and FeMgAl-NO₃.

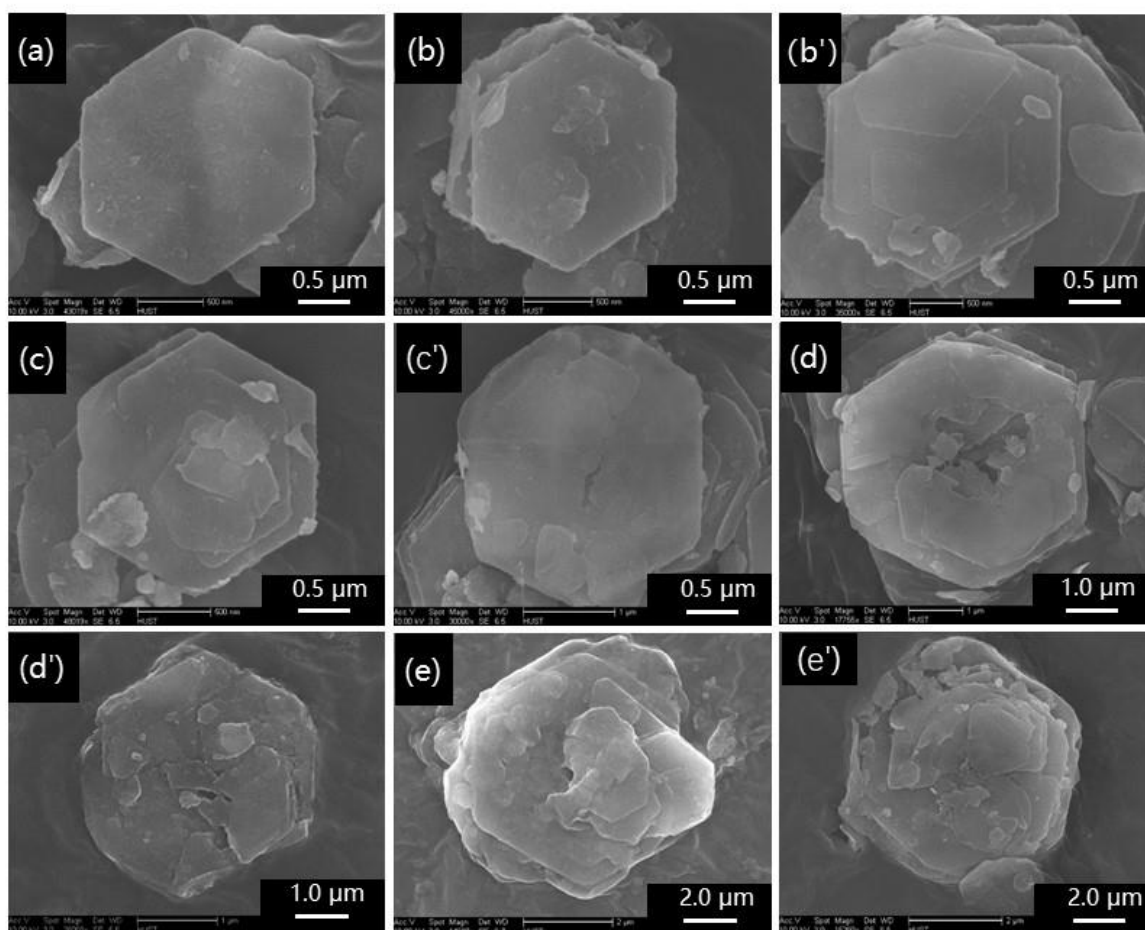


Supplementary Figure S4. Raman spectra of (NH₄)₂MoS₄ and FeMgAl-MoS₄.



Element	Wt%	At%
OK	14.60	31.44
NaK	01.89	02.83
MgK	04.32	06.12
SeL	28.82	12.58
PtM	07.92	01.40
SK	42.45	45.63
Matrix	Correction	ZAF

Supplementary Figure S5. SEM morphology and EDX profile of Se-adsorbed FeMgAl-MoS₄

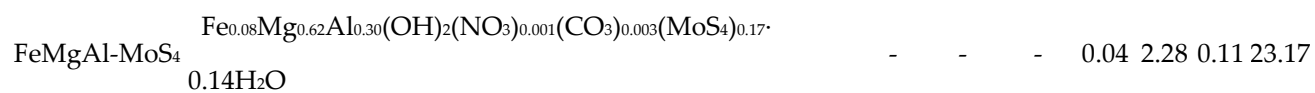


Supplementary Figure S6. SEM images of the original FeMgAl-MoS₄ adsorbents (a) and samples after FeMgAl-MoS₄ adsorbed of (b, b') 10 ppm Se(IV) and 10 ppm Se(VI), (c, c') 100 ppm Se(IV) and Se(VI), (d, d') 200 ppm Se(IV) and Se(VI), (e, e') 500 ppm Se(IV) and Se(VI).

2.1 Tables

2.1.1. **Table S1.** Elemental analysis, the chemical formula of synthesized LDH.

Adsorbents	Formula	Wt% calculated						
		%Fe	%Mg	%Al	%C	%H	%N	%S
MgAl-NO ₃	Mg _{0.67} Al _{0.33} (OH) ₂ (NO ₃) _{0.29} (CO ₃) _{0.02} ·0.45H ₂ O	-	27.61	11.34	0.28	2.91	4.09	-
MgAl-MoS ₄	Mg _{0.67} Al _{0.33} (OH) ₂ (NO ₃) _{0.02} (CO ₃) _{0.02} (MoS ₄) _{0.16} ·0.14H ₂ O	-	-	-	0.25	2.27	0.03	20.74
FeMgAl-NO ₃	Fe _{0.08} Mg _{0.62} Al _{0.30} (OH) ₂ (NO ₃) _{0.31} (CO ₃) _{0.01} ·0.41H ₂ O	6.16	22.08	12.15	0.12	2.82	4.34	-



2.1.2. **Table S2.** Comparison of MgAl-NO₃, FeMgAl-NO₃, MgAl-MoS₄, and FeMgAl-MoS₄ on selenite and selenate removal. (Phase ratio = 1.0 g/L, contact time = 24 hours, 25 °C, without adjustment of pHs).

Adsorbents	target	pH	initial(ppm)	final(ppm)	capacity(mg/g)
MgAl-NO ₃	Se(IV)	8.12	1068	953	115
MgAl-MoS ₄		8..35	1071	800	271
FeMgAl-NO ₃		8.34	1060	911	149
FeMgAl-MoS ₄		8.65	1072	588	484
MgAl-NO ₃	Se(VI)	7.86	583	524	59
MgAl-MoS ₄		7.53	581	494	87
FeMgAl-NO ₃		7.91	579	498	81
FeMgAl-MoS ₄		7.64	586	419	167

2.1.3. **Table S3.** Calculated values of maximum uptake capacities (q_m) for oxoanions calculated based on ion-exchange or S(-II) reduction or combined.

For only MoS_4^{2-}

This functional group leached by $(\text{NH}_4)_2\text{MoS}_4$, with a molecular weight (M)=260. Cause it can dissolve in water, therefore, it can assume that only reduction took place under these conditions.

If complete reduction:

For Se (IV), Se (IV) changed into Se (0) while S (-II) oxidized into S (VI), and 1 g S (-II) can reduce $1/32 \times 2 \times 78.96 = 4.9$ g Se (IV)

$$\text{So, } q_m = 1/260 \times 4 \times 32 \times 0.43 \times 4.9 = 1044 \text{ mg/g}$$

For Se (VI), we assumed Se (VI) changed into Se (0) for removal

$$\text{So, } q_m = 1044/3 \times 2 = 696 \text{ mg/g}$$

For MgAl- NO_3

The chemical formula of $\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{NO}_3)_{0.29}(\text{CO}_3)_{0.02} \cdot 0.45\text{H}_2\text{O}$,

With a molecular weight(M)=78.

If complete ion exchange:

For HSeO_3^- , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{HSeO}_3)_{0.33} \cdot 0.45\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/78 \times 0.33 \times 78.96 \times 1000 = 334 \text{ mg/g}$$

For SeO_3^{2-} , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{SeO}_3)_{0.165} \cdot 0.45\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/78 \times 0.165 \times 78.96 \times 1000 = 167 \text{ mg/g}$$

For SeO_4^{2-} , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{SeO}_4)_{0.165} \cdot 0.45\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/78 \times 0.165 \times 78.96 \times 1000 = 167 \text{ mg/g}$$

When pH 8.5, there are 37% HSeO_3^- and 63% SeO_3^{2-} in the solution, which means the calculated value is:

$$q_m = 0.37 \times 334 + 0.63 \times 167 = 229 \text{ mg/g}$$

When pH 7.5, there are 100% SeO_4^{2-} in the solution, which means the calculated value of Se(VI) is: $q_m = 167$ mg/g

For MgAl- MoS_4

The chemical formula of $\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{NO}_3)_{0.02}(\text{CO}_3)_{0.02}(\text{MoS}_4)_{0.16} \cdot 0.14\text{H}_2\text{O}$

With a molecular weight(M)=108.

If complete ion exchange:

For HSeO_3^- , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{HSeO}_3)_{0.38} \cdot 0.14\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/108 \times 0.38 \times 78.96 \times 1000 = 278 \text{ mg/g}$$

For SeO_3^{2-} , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{SeO}_3)_{0.19} \cdot 0.14\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/108 \times 0.19 \times 78.96 \times 1000 = 139 \text{ mg/g}$$

For SeO_4^{2-} , $\text{Mg}_{0.62}\text{Al}_{0.33}(\text{OH})_2(\text{SeO}_4)_{0.19} \cdot 0.14\text{H}_2\text{O}$ $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/108 \times 0.19 \times 78.96 \times 1000 = 139 \text{ mg/g}$$

When pH 8.5, there are 37% HSeO_3^- and 63% SeO_3^{2-} in the solution, which means the calculated value is:

$$q_m = 0.37 \times 278 + 0.63 \times 139 = 190 \text{ mg/g}$$

When pH 7.5, there are 100% SeO_4^{2-} in the solution, which means the calculated value of Se(VI) is: $q_m = 139$ mg/g

If complete reduction:

For Se (IV), Se (IV) changed into Se (0) while S (-II) oxidized into S (VI), and 1 g S (-II) can reduce $1/32 \times 2 \times 78.96 = 4.9$ g Se (IV)

$$\text{So, } q_m = 1/108 \times 4 \times 32 \times 0.16 \times 4.9 = 929 \text{ mg/g}$$

For Se (VI), we assumed Se (VI) changed into Se (0) for removal

$$\text{So, } q_m = 929/3 \times 2 = 619 \text{ mg/g}$$

For homogeneous Fe

With homogeneous Fe experiments, the proper amount of Fe (II) and Fe (III) was added into solution as the only iron source of the solutions.

For FeMgAl-NO₃

The chemical formula of $\text{Fe}_{0.08}\text{Mg}_{0.62}\text{Al}_{0.30}(\text{OH})_2(\text{NO}_3)_{0.31}(\text{CO}_3)_{0.01} \cdot 0.41\text{H}_2\text{O}$,

With a molecular weight(M)=89.

If complete ion exchange:

For HSeO_3^- , $\text{Fe}_{0.08}\text{Mg}_{0.62}\text{Al}_{0.30}(\text{OH})_2(\text{HSeO}_3)_{0.33} \cdot 0.41\text{H}_2\text{O}$, $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/89 \times 0.33 \times 78.96 \times 1000 = 293 \text{ mg/g}$$

For SeO_3^{2-} , $\text{Fe}_{0.08}\text{Mg}_{0.62}\text{Al}_{0.30}(\text{OH})_2(\text{SeO}_3)_{0.165} \cdot 0.41\text{H}_2\text{O}$, $M_{\text{Se}} = 78.96$

$$\text{So, } q_m = 1/89 \times 0.165 \times 78.96 \times 1000 = 146 \text{ mg/g}$$

When pH 8.5, there are 37% HSeO_3^- and 63% SeO_3^{2-} in the solution, which means the calculated value is:

$$q_m = 0.37 \times 293 + 0.63 \times 146 = 200 \text{ mg/g}$$

When pH 7.5, there are 100% SeO_4^{2-} in the solution, which means the calculated value of Se(VI) is: $q_m = 146 \text{ mg/g}$

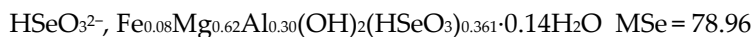
For FeMgAl-MoS₄

The chemical formula of $\text{Fe}_{0.08}\text{Mg}_{0.62}\text{Al}_{0.30}(\text{OH})_2(\text{NO}_3)_{0.001}(\text{CO}_3)_{0.01}(\text{MoS}_4)_{0.17} \cdot 0.14\text{H}_2\text{O}$,

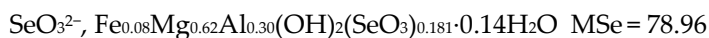
With a molecular weight(M)=103.

If complete ion exchange:

For Se(IV),

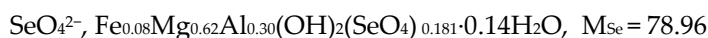


$$\text{So, } q_m = 1/103 \times 0.361 \times 78.96 \times 1000 = 277 \text{ mg/g}$$



$$\text{So, } q_m = 1/103 \times 0.181 \times 78.96 \times 1000 = 139 \text{ mg/g}$$

For Se(VI),



$$\text{So, } q_m = 1/103 \times 0.181 \times 78.96 \times 1000 = 139 \text{ mg/g}$$

When pH 8.5, there are 37% HSeO_3^- and 63% SeO_3^{2-} in the solution, which means the calculated value of Se(IV) is: $q_m = 0.37 \times 277 + 0.63 \times 139 = 190 \text{ mg/g}$

When pH 7.5, there are 100% SeO_4^{2-} in the solution, which means the calculated value of Se(VI) is: $q_m = 139 \text{ mg/g}$

If complete reduction:

For Se (IV), Se (IV) changed into Se (0) while S (-II) oxidized into S (VI), and 1 g S (-II) can reduce $1/32 \times 2 \times 78.96 = 4.9 \text{ g Se (IV)}$

$$\text{So, } q_m = 1/103 \times 4 \times 32 \times 0.17 \times 4.9 = 1035 \text{ mg/g}$$

For Se (VI), we assumed Se (VI) changed into Se (0) for removal

$$\text{So, } q_m = 1035/3 \times 2 = 690 \text{ mg/g}$$

2.1.4. Table S4. Sorption isotherms of Se(IV) on FeMgAl-MoS₄. (Phase ratio = 1.0 g/L, contact time = 24 hours, 25 °C, without adjustment of pHs).

C ₀ (ppm)	C _f (ppm)	removal (%)	initial pH	final pH	Mo C _f (ppm)	q _e (mg/g)	K _d (mL/g)
10	0	99.2	7.9	7.1	2.5	9.9	1.24×10 ⁵
20	0	98.2	8.1	7.2	9.8	19.6	5.31×10 ⁴
51	2	96.8	8.1	7.4	20.5	49.4	3.09×10 ⁴
98	10	90.2	8.3	7.8	47.2	88.4	9.21×10 ³
205	36	82.4	8.3	8.0	62.3	169.0	4.69×10 ³
516	195	62.2	8.4	8.1	101.5	321.0	1.65×10 ³
1072	588	45.2	8.7	8.1	117.6	484.0	0.82×10 ³