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COMMUNICATION
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N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+, X = S, Se, Te)

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Metal-sulfide/Polysulfide Functionalized Layered Double Hydroxides – Recent Progress in the Removal of Heavy Metal Ions and Oxoanionic Species from Aqueous Solutions

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Abstract

Water constitutes an indispensable resource for global life but remains susceptible to pollution from diverse human activities. To mitigate this issue, researchers are committed to purifying water using a variety of materials to remove harmful chemicals, such as heavy metals. Layered double hydroxides (LDHs), with their intriguing, layered structure and chemical behavior, have attained substantial attention for their effectiveness in removing heavy metal ions and various inorganic oxoanions from water. To enhance efficiency, considerable endeavors have focused on functionalizing LDHs with different chemical species. Intercalation with metal sulfides has proven to be particularly effective, facilitating heavy metal absorption through multiple mechanisms, including ion-exchange, reductive precipitation, and surface sorption. This review concentrates on the synthesis, and performance of polysulfides (S_x, x = 2-5), Mo-S, and Sn-S anions intercalated LDHs for heavy metals and inorganic oxoanions sorption, along with their adsorption mechanisms. Furthermore, the discussion includes prospects for expanding the chemistry of metal sulfides intercalated LDHs, along with existing challenges and future outlooks.

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1. Introduction

At present, over one billion people worldwide face challenges in accessing clean and decontaminated drinking water.[1] According to the World Health Organization (WHO), by 2050, this issue is expected to escalate, affecting nearly six billion people globally.[2] Hence, the exponential increase in the water crisis is directly related to population and industrial growth. Heavy metals, such as cadmium, zinc, silver, lead, copper, and mercury, remain in wastewater, and their improper discharge severely contaminates ecosystems, posing risks to biological systems.[3–5]

Over the last decades, various physical and chemical methods, such as filtration,[6,7] coagulation-flocculation,[8,9] precipitation,[10,11] ion exchange,[12,13] adsorption,[14,15] electro-catalytical,[16–19] and photocatalytic techniques[20] have been developed for the removal of heavy metals from contaminated water. Chemical separations allow trace-level removal of heavy metal ions besides achieving superior selectivity and faster kinetics. Among these, adsorption, ion exchange, and (reductive) precipitation mechanisms have garnered widespread attention across a diverse array of materials, including activated[21–23] and sulfur-impregnated carbon,[24–26] zeolites,[27–29] metal-organic frameworks,[30–32] layered metal-sulfides,[33] clay minerals,[34–36] various organic molecules,[37–39] and organic-inorganic composite materials.[40–43]

Layered double hydroxides (LDHs) are two-dimensional (2D) anionic clay, typically described by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M and A represent metals and interlayer anions, respectively.[23,44–48] The intriguing two-dimensional cationic layered structure of LDHs, along with their tunable elemental composition and exchangeable anions, draw attention to them. These features allow for the modification of their physicochemical properties, resulting in a variety of sorption mechanisms, such as surface adsorption, interlayer anion exchange, and topotactic exchange of the layered cations.[49–51] In particular, the LDHs are a great option for heavy metal sorption because of their flexibly tunable metal cations, which provide a super-stable mineralization effect that immobilizes absorbed heavy metals in the interlayers.[49] Additionally, because of their massive OH^- ion content, LDHs are extremely rich in heavy metal binding sites.[,52] The LDH layer reconstruction also facilitates the removal of various heavy metal ions and oxoanions from wastewater.[45,53–56] However, without functionalization, LDHs suffer from low selectivity and adsorption capability, thus limiting their potential for effectively removing heavy metal ions. Functionalizing LDHs can be achieved by four distinct methods namely defect

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engineering, intercalation, surface functionalization, and nanocomposites.[57] Amongst, by intercalating sulfide-based materials gained major attention as it exhibit exceptional affinity towards heavy metal ions and selectively bind Lewis acidic soft heavy metal ions according to Pearson's hard-soft Lewis acid-base principles (HSAB).[58–66,67–74] Although, LDH exhibits good performance for the sorption of heavy metal ions, without functionalization their sorption of heavy metal ions is not up to the mark. Thus, the integration of sulfide species, such as polysulfides and metal sulfides, with LDHs results in a hybrid LDH-metal sulfide structures that collectively integrate the synergic sorption properties of metal sulfides and LDHs, offering a new paradigm for the synthesis of high-performing materials for the separation of heavy metal ions and oxoanions from water.[75]

2. Scope of the review

Over the past decade, numerous publications have explored the synthesis of various polysulfides and metal-sulfide functionalized LDHs, investigated their sorption properties in heavy metal cations and oxoanions, and analyzed the sorption mechanisms. Consequently, these studies have had a significant impact on the field of hybrid 2D LDH-metal sulfide synthesis and their applications in wastewater purification by removing heavy metal cations, oxoanionic species, and separation of radioactive ions. This paper aims to discuss design principles for the functionalization of LDHs and analyze the roles of various interlayer metal sulfide anions and layered cations and their impact on the separation of chemically diverse pollutants from water and gases. These efforts are expected to contribute to ongoing innovation in this promising materials and environmental chemistry field.

3. General Synthetic Strategies of Meta-sulfide Intercalated LDHs

LDH offers a robust chemical composition with both layer cations and interlayered anions.[76,77] While the layered cations vary from s, p, d, and f block metal ions, the interlayered anions vary to include halides, inorganic oxoanions, and organic anionic species.[78–80] The synthesis of such a robust class of chemically diverse compositions involves versatile synthetic approaches, including co-precipitation,[81] hydrothermal,[82] sol-gel,[83] electrodeposition[84] and other.[85–87]

The inter-layer anion exchange process of LDH represents a well-established technique for intercalating both organic and inorganic anions, however, the anion exchange phenomena are

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related to the affinity of the anions to the LDH layers. For instance, according to Miyata the affinity of the LDH toward various anions is in the following order: CO_3^{2-} >SO_4^{2-} >OH^- >F^- >Cl^- >Br^- >NO_3^- >I^-.[88] Importantly, the exchange of CO_3^{2-} is extremely difficult to ion exchange but under acidic conditions CO_3^{2-} anions can be protonated and subsequently be deintercalated by less affinitive anions, such as Cl^-, and NO_3^- toward LDH layers.[88,89] Importantly, the ion exchange property may facilitate an anion with higher anion charge and smaller ionic sizes. The intercalation of metal sulfides or the polysulfide anions into LDH should not be as favorable oxoanions or halide species because of the poor affinity of sulfide anions toward LDH layers. This could be understood by simple consideration of HSAB principle.[89]

Ma et al.[90, 103] reported the ion-exchange of polysulfide anions, $(S_x)^{2-}$ or metal sulfide (MoS_4^{2-}) by the nitrate of the MgAl-NO_3-LDH. Hence the ion-exchange needs an excessive amount of $(S_x)^{2-}$ or metal sulfide (MoS_4^{2-}), which may be because of the requirement of creating chemical pressure to enforce polysulfide/metal sulfide anions going into to the LDH layers, however, the reason is not established. The excessive unreacted metal sulfides, beyond the stoichiometry of LDH-S_x/M_xS_y ($M_xS_y \equiv MoS_4^{2-}$, Mo_3S_{13}, SnS_4^{4-}, and $Sn_2S_6^{4-}$), are removed by washing after the intercalation process. Hence the intercalation of polysulfide and / metal sulfides, such as M_xS_y was achieved by stepwise ion exchange of the LDH─CO_3 → LDH─NO_3 → LDH─S_x/M_xS_y, as depicted in the figure 1A. Hence, the ion-exchange of CO_3 to NO_3 requires acidic media to create less affinitive proportionated carbonate and can subsequently be exchanged with NO_3^- that remains in solution in excessive amounts. In step 2, NO_3^- of the LDH-NO_3 was exchanged with the metal sulfide anion M_xS_y to produce LDH─ S_x/M_xS_y in solutions.

Another approach involves delaminating LDHs in polar organic solvents, such as dimethyl formamide and formamide, subsequently restacking the positively charged layer by metal sulfide anions.[91] In particular, Celik *et al* showed the synthesis of LDH─Mo_3S_{13} by exfoliating the MgAl-LDH for 24 h in formamide to delaminated LDH layers.[92] During the delamination process, solvent molecules replace the interlayered anions leading to an increase of the interlayered spaces. The delaminated LDHs were then introduced to the Mo_3S_{13} anions which gradually allowed the positively charged layers to restack to produce Mo_3S_{13} functionalized LDH, as shown the Figure 1B. This approach is particularly suitable for bulky thiosulfide anions.

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Overall, the intercalation chemistry of metal sulfide into LDH layers involves several factors, including M^{2+}/Mo^{3+} ratio, charge density of the host layers, interlayer spaces, crystallinities, interlayer water, pH of the solution, besides the size, charge entities and geometry of metal sulfides.[93,94] These phenomena offer particular challenges for specific LDH and metal sulfide anions.

The intercalation chemistry of metal-sulfide into LDH can be understood by X-ray powder diffraction from the shift of the d_{003} basal space of LDH (Figure 1C). In general, intercalation of a larger polysulfide of metal-sulfide anion expands the unit cell along the *00l* crystallographic planes. Besides, FTIR spectroscopy is another vital method that demonstrates interlayered anion exchange phenomena. For example, the CO_3^{2-} and NO_3^-ions are responsible for the peak at 1355 cm^{-1} (Figure 1D This peak entirely vanishes following the intercalation of MoS_4, indicating a successful intercalation. Consequently, FTIR and XRD become the most common and useful methods to confirm the intercalation of metal sulfide ions into the interlayered spaces of the LDHs. Besides, the presence of the intercalated species can be commonly identified by energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. For instance Celik et al.[48] intercalated Sn_2S_6 into the MgAl-LDH layers and to confirm the presence of Sn_2S_6 anions in the interlayer XPS survey spectra were recorded. In figure 1E the intense peaks for the Sn and S were obviously seen after intercalation at the binding energy range of 482-495 eV and 157-163 eV respectively. These two characteristic peaks confirm the existence of the Sn_2S_6 at the LDH interlayers and depict that the XPS survey spectrum can be an effective tool for identifying the existence of intercalated anions in the LDH layers.

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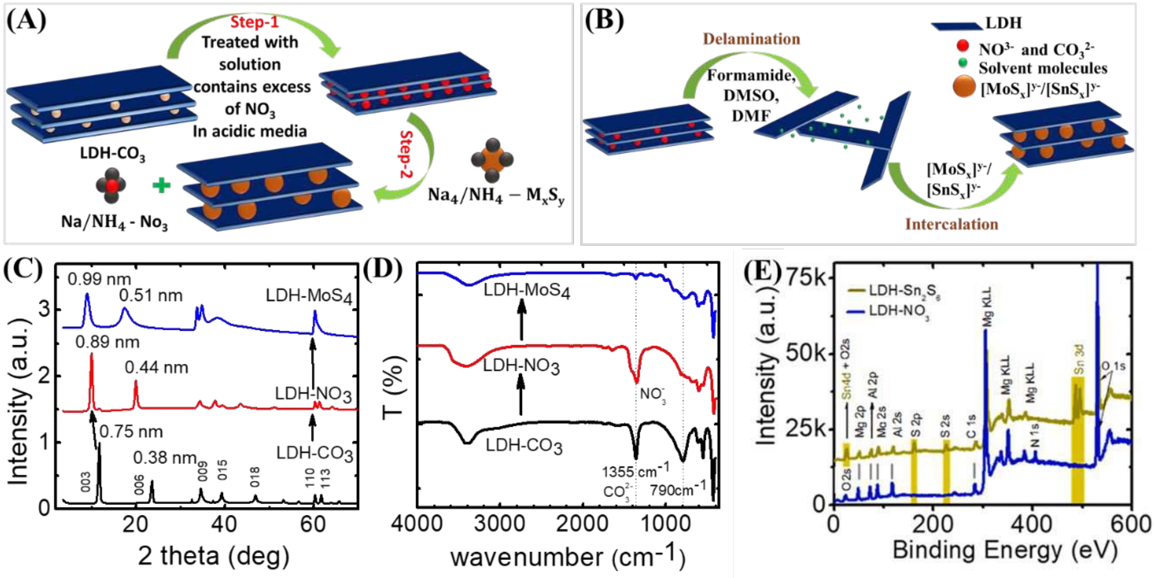

Figure 1: Schematic representation of intercalation process of sulfide anions into LDHs by (A) anion exchange method, (B) delamination-restacking method, Comparable features of CoAl-CO_3, CoAl-NO_3, and CoAl-MoS_4 (C) PXRD patterns showing the shift of diffraction peaks to the lower diffraction angles according to the increasing size of the intercalated anions of CO_3^{2-}, NO_3^-, and MoS_4^{2-}; (D) FT-IR spectra show abolishing of vibration frequency of CO_3^{2-} and NO_3^- due to intercalation of [MoS_4^{2-}] confirm the formation of CoAl-[MoS_4] reprinted with permission from *Roy et al.*[95] copyright 2022 Taylor & Francis online and (E) XPS survey spectra LDH-NO3 and LDH-Sn2S6 reprinted with permission from *celik et al.* [48] copyright 2021 Elsevier.

4. Removal of heavy metal ions

To date, LDH was functionalized with polysulfides (S_x; x=3-6), molybdenum sulfides, (MoS_4^{2-} and Mo_3S_{13}), and tin sulfides (SnS_4^{4-}, and $Sn_2S_6^{4-}$) anions and were studied in the environmental remediation pursuit.[96–102] Hence, the remediation includes heavy metal cations and oxoanionic species of metals, arsenic and selenium, and gaseous mercury and radioiodine. Since the discovery of sulfides/metal-sulfides functionalized in the past decade, this class of materials has received paramount attention because of their remarkable sorption capacity and efficiencies for heavy metals cations and oxoanionic species, as summarized in Table 1.[103]

4.1. Polysulfide Intercalated LDHs

Polysulfide intercalated layered double hydroxides (LDHs) represent a versatile and effective class of materials for environmental remediation, particularly in the capture and removal of heavy metals, mercury vapor, iodine vapor, and uranium from contaminated environments.[104–106] These

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LDHs utilize the unique chemical properties of polysulfides, which are intercalated within the layered structure of the hydroxides, to selectively bind and sequester these hazardous substances, as stated above. Ma *et al.* unveiled the high sorption efficiency of polysulfides intercalated Mg/Al LDHs (S_x-LDH) for metals ions, including Cu(II), Ag(I), and Hg(II) and uranium as UO_2^{2+}.[106] They show great affinity to bind with highly toxic mercury, having been able to reduce concentrations from ppm to trace (≤10 ppb) levels. The S_x-LDH materials had higher selectivity for Cu(II)/Zn(II) than for Co(II)/Ni(II) and provided good separation of these transition metal ions. S_2-LDH, the uptakes for Hg(II), Pb(II), Ag(I), Zn(II), and Cu(II) are 686, 483, 383, 145. and 127 mg/g, respectively. In another research work, S_x-LDH materials demonstrate highly selective UO_2^{2+} removal in both aqueous solution and seawater.[105] The maximum removal capacities of both S_4-LDH and S_2-LDH were calculated to be ~330 mg/g in aqueous solutions, which are comparable to other high-performing materials.[107–109] The materials showed high uranium removal percentages and excellent affinity for UO_2^{2+} with K_d values up to 3.4×10^6 mL/g. S_x-LDH are able to selectively bind to uranium even in the presence of other competing ions like calcium and sodium. Overall, the findings support the potential of S_x-LDH as an effective sorbent for heavy metal cations, and oxo-cationic species.

4.2. Molybdenum Sulfide Intercalated LDHs

MoS_4^{2-} anion intercalated layered double hydroxides (LDHs) become very efficient and selective adsorbents for heavy metal removal from wastewater[90,110-112]. Figure 2A shows the sorption kinetic of MgAl-MoS_4-LDH material that displays remarkable selective binding and efficient removal of heavy metal ions, such as Cu(II), Pb(II), Ag(I), and Hg(II) and their corresponding capacities are 181, 289, 450 and 500 mg/g respectively.[90] The material was found to effectively capture heavy metal ions, with its selectivity order being Co(II), Ni(II), Zn(II) < Cd(II) ≪ Pb(II) < Cu(II), Hg(II), Ag(I).[90] These LDHs, particularly FeMgAl-MoS_4 (Fe-MoS_4-LDH), have high adsorption capabilities of 582 mg/g for Hg(II) and 565 mg/g for Ag(I), with rapid kinetics.[110] The redox-active metals, such as Mn into the MgAl-LDH structure and the intercalation with MoS_4^{2-} anions (as referred Mn-MoS_4-LDH), demonstrated selectivity of Co(II), Ni(II), Zn(II) < Cd(II), Cu(II), < Hg(II), Pb(II), Ag(I) and maximum removal capacity of 594, 564, and 357 mg/g for Hg(II), Ag(I) and Pb(II), respectively.[111] Another research work showed the formation of MoS_4^{2-} intercalated NiFeTi-LDH and its effectiveness for the removal of toxic $Pb^{(II)}$ and Ag^+ ions (adsorption

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capacities of 653 mg/g for Pb(II) and 856 mg/g for Ag(I) metal ions).[112] In their work, the responses toward various metal ions were listed in the following order: Ni(II) < Cu(II) < Zn(II) < Fe(III) <Pb(II) < Ag(I). Introducing redox-active 3d transition metals into the MgAl-LDH structure and intercalating with MoS_4^{2-}anions could modulate the charge density of metallic layers and ion-exchange features. These ultimately could affect the stability of intercalated MoS_4^{2-}anions as well as efficiency in the removal of heavy metal ions from water.

Apart from this, He et al. reported CaAl-LDHs (LDH-MoS_4) for the removal of Pb(II) and Cd(II).[113] The obtained LDH-MoS_4 nanocomposites demonstrated enormous adsorption capacities of 1202.1 and 678.3 mg/g for Pb(II) and Cd(II), respectively.[113] The authors concluded that strong M-S covalent bonds between the heavy metals and $[MoS_4]^{2-}$ clusters, as well as the lattice substitution of Cd(II) with Ca(II) on the LDHs layer due to similar ionic radii, contribute to the efficient adsorption.

Apart from MoS_4^{2-} intercalated LDH, $Mo_3S_{13}^{2-}$ - intercalated LDH stands out as a promising material. The presence of $Mo_3S_{13}^{2-}$ anions within the LDH matrix facilitates selective anion exchange mechanisms, crucial for capturing anionic heavy metal species. Moreover, the reduction capability of $Mo^{(IV)}$ and S_x^{2-} in $Mo_3S_{13}^{2-}$ anions enables the transformation of heavy metals into less toxic forms, improving the efficiency of remediation processes.[91] Yang et al. synthesized $Mo_3S_{13}^{2-}$ intercalated MgAl-LDHs (Mo_3S_{13}-LDH), an exceptionally potent nanosorbent for heavy metals.[91] Notably, it exhibited exceptional efficacy in the removal of Ag^+ ions, boasting a maximum adsorption capacity of 1073 mg/g. Furthermore, Mo_3S_{13}-LDH has exceptional selectivity towards heavy metals, with a special affinity for, among others, Hg(II), Cu(II), and Pb(II). It is noteworthy that the substance retains an efficiency of >99.9 percent in eliminating Ag(I) ions as metallic Ag, even in situations where Cu(II) concentrations are high. This indicates the potential of Mo_3S_{13}-LDH for precious metal extraction.

In the realm of environmental remediation, the innovation of making composite materials of MoS_4-LDH, as exemplified in recent studies, offers a significant advancement in the removal of heavy metals from water. The introduction of porous carbon foam and magnetic Fe_3O_4 to LDHs significantly enhances their capability for heavy metal removal. Porous carbon foam offers a high surface area and structural support besides their intrinsic affinity to metal cations and thus its integration with metal-sulfide LDH to enhance sorption capacity for metal ions. Wang *et al.*

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proposed a NiFe-MoS_4^{2-}- LDH/CF hybrid monolith that is found to be highly effective for the sequestration of Hg(II), Pb(II), and Cu(II), exhibiting ultrahigh sorption capacities of 462, 299, and 128 mg/g, respectively.[96] By loading $FeMoS_4$ onto protonated F_3O_4 adhered to the surface of MgAl-LDH, Elham *et al.* explored a nanosorbent for Pb(II), Cd(II), and Cu(II) with significant adsorption capabilities and superior regeneration and reusability feature.[114] The aforementioned studies illustrate notable progressions in LDH technology using intercalation of anions bearing MoS_4^{2-} and $Mo_3S_{13}^{2-}$. This intercalation improves the capacity, selectivity, and efficacy of heavy metal ion adsorption from wastewater. Moreover, the integration of structural and magnetic advancements in hybrid composites holds great potential for future utilization in the field of environmental remediation.

4.3. Tin Sulfide Intercalated LDHs

Beyond molybdenum sulfides LDH, Sn-S intercalated LDH presents a stimulating opportunity for thioanion intercalated LDHs to separate heavy metal ions from wastewater. These materials also present an outstanding extension of metal sulfide functionalized LDH nanosorbent for heavy meats. Specifically, $Sn_2S_6^{4-}$ and SnS_4^{4-} intercalated LDHs exhibit high affinity toward soft heavy metal ions.[98,100,115] Celik *et al.* described the intercalation of $Sn_2S_6^{4-}$ into the gallery of MgAl-LDH (LDH-Sn_2S_6) and showed unprecedented removal efficiency of heavy metal cations of Cu(II), Ag(I), Cd(II), Pb(II), and Hg(II) as shown in the kinetic curves (Figure 2B) below the WHO limit for drinking water.[98] The soft polarizable Lewis basic properties of the sulfides (S^{2-}) of the thiostannate anions in this hybrid LDH–[Sn_2S_6] nanosheets enable a vast array of Lewis acidic heavy metal cations to be absorbed with a high degree of selectivity. LDH-[Sn_2S_6] can absorb Cu(II), Ag+, Cd(II), Pb(II), and Hg(II) with extremely high capacity, and their maximum sorption capacities were obtained 378, 978, 332, 579, and 666 mg/g, respectively. MgAl-LDHs supported SnS_4^{4-} clusters were reported by Chen *et al*. show 99% Hg(II) removal efficiency under low pH values. This nanosorbent shows selectivity on Hg(II) removal in the presence of coexisting metal ions, such as Zn(II), Na+, Cd(II), Cr(III), Pb(II), Co(II), and Ni(II).[115] Besides, Li *et al.* demonstrated that SnS_4^{4-} modified MgFe-LDH composite exhibited excellent mercury and arsenic removal.[100] The authors reported that the elimination of arsenic was mostly attributed to the presence of the Fe site in the LDH composite, As-O-Fe bond formed during the adsorption of As(III), whereas the uptake of mercury was attributed to the SnS_4^{4-}clusters sites. These

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developments in Sn-S intercalated LDHs demonstrate the great potential of thioanion-based nanosorbents for the selective and effective removal of heavy metals from wastewater, paving the way for future water treatment technologies.

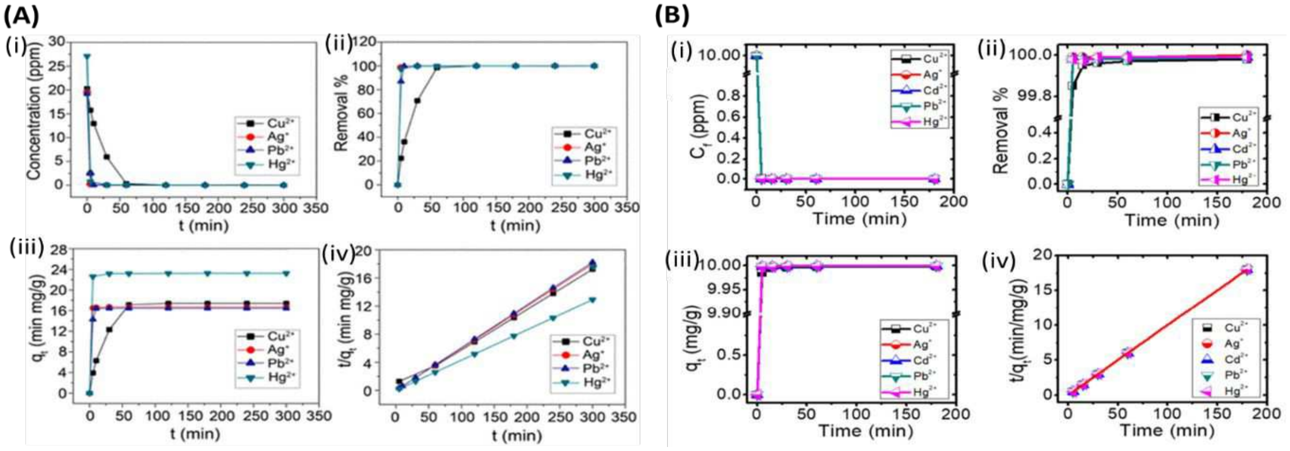

Figure 2. Heavy metal adsorption kinetics curves of (A) LDH-MoS_4, reprinted with permission From Ma *et al.*[116] copyright 2016 American Chemical Society and (B) LDH-Sn_2S_6, reprinted with permission From Celik *et al*.[98] copyright 2021 Elsevier (where, (i) Ion concentration change with contact time, (ii) Removal % as a function of contact time, (iii) Sorption capacity (q_t) with contact time, and (iv) pseudo-second-order kinetic plots).

4.4. Metal Sulfide/Polysulfides intercalated LDH for Mercury/Iodine Vapor Capture

Considering the potential for extensive pollution as well as the toxicity of Hg and I_2 vapors, their presence in the environment presents a significant obstacle that demands inventive approaches to eliminate them. Iodine vapors, while less prevalent, provide threats in situations such as nuclear accidents; mercury emissions, specifically those stemming from industrial activity, can result in enduring environmental and health risks.[97,104,117,118] S_x-LDH showed a high efficiency towards Hg vapor capture. The formation of strong S-Hg-S bonds, driven by the S-S bonds of the polysulfides in the interlayer space, plays a significant role in Hg capture.[104] The polysulfide remaining S^{2-} undergoes oxidation to SO_4^{2-} and subsequently form SO_4-LDH. Hg capture capacities of S_2-LDH, S_4-LDH, and S_5-LDH are reported to be very high at 5.0×10^5, 7.6×10^5, and 1.0×10^6 μg/g, reaching 50-100% adsorption capacity by weight. Besides, an excellent Hg^0 removal efficacy was demonstrated by $[MoS_4]^{2-}$/CoFe-LDH at both low and high SO_2 concentrations, suggesting its

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potential for use in S-Hg mixed flue gas purification. S_x-LDH displays highly efficient iodine capture resulting from reducing the property of the intercalated polysulfides.[119]

The I_2 molecules are reduced to I_3^- ions while the polysulfide ions oxidize to form S_8. Similarly, S_2^{2-}/S^{2-} in $[Mo_3S_{13}]^{2-}$ can reduce the I_2 to $[I_3]^-$ ions, and thus subsequently be trapped within the LDH gallery through electrostatic attraction. Meanwhile, the S_2^{2-}/S^{2-} themselves are oxidized to S_8 and SO_4^{2-}, while Mo(IV) is oxidized (by O_2 in air) to Mo(VI), which combines with SO_4^{2-} forming amorphous molybdenum sulfates.[97] With a cooperative interaction of chemical and physical adsorption, the Mo_3S_{13}-LDH demonstrates a large iodine adsorption capacity of 1580 mg/g; whereas Sn_2S_6-LDH showed an extremely large iodine capture capacity of 2954 mg/g with a large contribution from physisorption.[117] For iodine in solutions, Sn_2S_6-LDH also shows excellent capture performance with an adsorption capacity of 1308 mg/g.[97,117] These findings demonstrate the importance of intercalated LDH-based adsorbents in environmental cleanup, capturing and neutralizing mercury and iodine through complex chemical processes and high-efficiency adsorption.

4.5. Metal Sulfide intercalated LDHs for Removal of Oxoanionic Species

Functionalizing the LDH with metal sulfide-based anions enhances the capture efficiency various oxoanionic species, such as SeO_4^{2-}, SeO_3^{2-}, $HAsO_3^{2-}$, $HAsO_4^{2-}$ attributed by the synergic effect of positively charged hydroxide layers with interlayer sulfide guests.[56] This occurs the complementary effect of electrostatic attraction between the cationic LDH layers and the desired anions, as well as covalent interactions between S-Cr, S-Se and S-As. Celik et al. reported the application of LDH-Mo_3S_{13} for the removal of CrO_4^{2-} as a redox surrogate for TcO_4^-, removes CrO_4^{2-} from the LAW condensate stream solution with a K_d value up to 10^7 mL/g and the kinetic properties can be observed from Figure 3.[92] This study unveiled that cooperative oxidation of molybdenum and sulfur enhances the reduction of highly soluble Cr(VI) to insoluble Cr(III) species. In another work, Celik et al. introduced an efficient sorbent LDH-Sn_2S_6 for ReO_4^-, an isostructural and isoelectronic surrogate for TcO_4^- from aqueous solution.[102] LDH-Sn_2S_6 exhibited a removal of ReO_4^- through multiple sorption processes, including anion exchange, surface sorption, and reductive precipitation. However, the authors noted that ion-exchange of the Sn_2S_6 anions by ReO_4^- is the dominant mechanism, while a trace amount of reduced Re(IV) species was found in the post-sorbed solids that could be attributed to the oxidation sulfides of the Sn_2S_6 ions.

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In contrast, LDH-Mo_3S_{13} almost exclusively follows reductive precipitation of chromate by reducing Cr(VI) to insoluble Cr(III) species. The distinction between LDH-Sn_2S_6 and LDH-Mo_3S_{13} is attributed to the presence of disulfide (S_2^{2-}) species in the Mo_3S_{13} anions, which is better described by $Mo_3S(S_2)_6$, of LDH-Mo_3S_{13} and the absence of (S_2^{2-}) in the Sn_2S_6 ions in the former. Zhang et al. found in another study that the Mo_3S_{13}-LDH adsorbent has a significant absorption value for Ag(I) (446.4 mg/g), Hg(II) (354.6 mg/g), As(III) (61.8 mg/g), and Cr(VI) (90.6 mg/g), demonstrating a good removal capacity for such a diverse range of ions. By adding Mo_3S_{13} to the LDH gallery, the interlayer gap widens, speeding up mass transfer and improving adsorption capacity.[120]

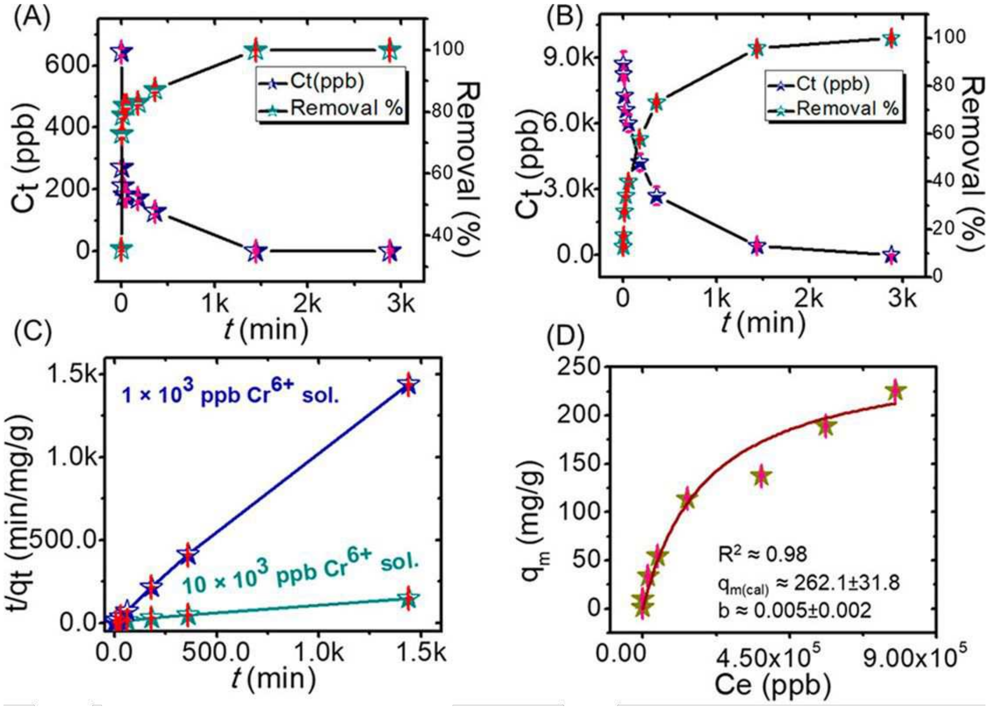

Figure 3. (A) Adsorption kinetics for the residual concentrations (C_t) and removal rates of Cr(VI) for 1.0 × 10^3 ppb and (B) 1.0×10^4 ppb solutions in DIW; (C) a comparison of the pseudo-second-order adsorption kinetics for 1×10^3 and 1×10^4 ppb solutions; (D) adsorption capacity (q_m) vs equilibrium adsorption concentrations (C_e). Reprinted with permission From Celik *et al.*[92] copyright 2022 American Chemical Society.

Ma et al.[56] reported, MoS_4-LDH as highly efficient sorbent of various oxoanions, including $HAsO_3^{2-}$, $HAsO_4^{2-}$, SeO_4^{2-}, $HSeO_3^{2-}$ and CrO_4^{2-}. Specifically, MoS_4-LDH shows a very high removal rate (>99%) of As(III), As(V), and As(VI) from complex aqueous solutions, with remarkable selectivity for $HAsO_3^{2-}$, $HAsO_4^{2-}$, and CrO_4^{2-} in the presence of competing nontoxic

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anions. The material can rapidly reduce As(III) and Cr(VI) concentrations to <10 ppb, below the permitted level for drinking water. The maximum adsorption capacities for As(III), As(V), and Cr(VI) are 99, 56, and 130 mg/g, respectively. In contrast, Roy et al. reported CoAl-MoS_4-LDH that can effectively remove CrO_4^{2-} from acidic, neutral, and basic media with a removal capacity as high as 231 mg/g.[95] The authors also reported that adsorptions of As(V) and Cr(VI) are exceptionally rapid, with >93% and >96% removal within 1 min and 5 min, respectively. In another study, Ma et al. reported that the presence of transition metal ions, such as $Hg^{(II)}$, $Cu^{(II)}$, and $Cd^{(II)}$ accelerates the capture of selenium oxoanions.[101] It was found that the MoS_4-LDH material demonstrated excellent performance in comparison with NO_3^- intercalated LDHs in the simultaneous removal of toxic Se(VI)/Se(IV) oxoanions and heavy metals (Hg(II), Cu(II), and Cd(II)) as shown in kinetic curves (Figure 4).[121] The maximum sorption capacities for individual Se(VI) and Se(IV) were 85 and 294 mg/g, respectively.

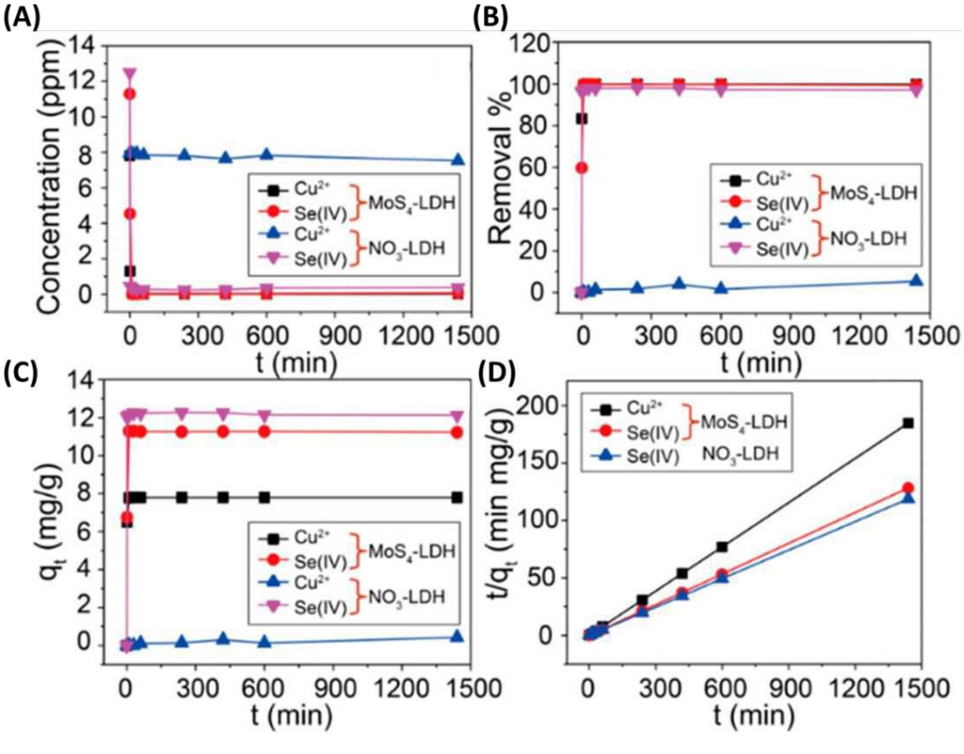

Figure 4. Sorption kinetics curves for Se(IV) and Cu(II) by MoS_4-LDH and NO_3-LDH: (a) Concentration change following contact time, (b) removal % as a function of contact time, (c) sorption capacity (qt) with contact time, and (d) pseudo-second-order kinetic plots for the sorption; Reprinted with permission From Ma *et al.*[101] copyright 2017 American Chemical Society.

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Liao *et al.* discussed the environmental implications of introducing MoS_4^{2-} groups into FeMgAl-LDH for the removal of selenium oxoanions from the environment.[45] The study found that the introduction of MoS_4^{2-} groups led to significant changes in the characteristics of the LDHs compared to other compounds. It was observed that the remaining selenium species in the solution could be reduced by leaching S^{2-}, resulting in the formation of Se(0) and SO_4^{2-}. Additionally, Fe from the LDH layers acted as catalysts for selenium reduction in chemical reactions. These findings show that metal sulfide intercalated LDHs are a strong and selective way to clean water of harmful oxoanions.

Table 1. Polysulfides/metal sulfides functionalized LDHs and their efficiency in the removal of various cations and anions.

Adsorbent	Heavy metal ion	Capacity (mg/g)	C_0, C_e (mg/L)	Ref
S_2-LDH	Hg(II)	686	2185, 814	[104–106]
	Ag(I)	383	767, 0.11	
	Pb(II)	483	1960, 1073	
	Zn(II)	145	615, 324	
	UO_2^{2+}	330	1478, 1148	
	Hg^0	5.0×10^5	-	
S_4-LDH	UO_2^{2+}	332	1478, 1146	[104,105]
	Hg^0	7.6×10^5	-	
MgAl-MoS_4-LDH	Hg(II)	500	500, 0.207	[90]
	Ag(I)	450	1484, 958	
	Pb(II)	289	1040, 751	
	Cu(II)	181	2223, 2012	
FeMgAl-MoS_4-LDH	Hg(II)	582	1000, 417.2	[110]
	Ag(I)	565	1000, 434.6	
Mn-MoS_4-LDH	Hg(II)	594	-	[111]
	Ag(I)	564	-	
	Pb(II)	357	-	
NiFeTi- MoS_4-LDH	Pb(II)	653	100,0 0.43	[112]
	Ag(I)	856	100,0 0.001	
Fe_3O_4-$FeMoS_4$-MgAl-LDH	Pb(II)	191	300, 14	[114]
	Cd(II)	141	300, 89.3	
	Cu(II)	110	300, 13.4	
NiFe-MoS_4^{2-}- LDH/CF	Hg(II)	462	-	[96]
	Pb(II)	299	-	
	Cu(II)	128	-	

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CaAl-MoS_4-LDH	Pb(II)	1202	-	[113]
	Cd(II)	678	-	
CoAl-MoS_4-LDH	CrO_4^{2-}	231	500, 269	[95]
Mo_3S_{13}-MgAl-LDH	Hg(II)	594	594, 0.04	[91]
	Ag(I)	1073	1662, 589	
LDH-Mo_3S_{13}	CrO_4^{2-}	225	1000,775	[99]
LDH-MoS_4	CrO_4^{2-}	130	167, 36	[56,121]
	As(III)	99	341, 242	
	As(V)	56	306, 250	
	Se(VI)	85	316, 231	
	Se(IV)	144	534, 240	
LDH-Sn_2S_6	Hg(II)	666	1500, 834	[117]
	Pb(II)	579	1500, 921	
	Cd(II)	332	1500, 1168	
	Ag(I)	978	1500, 522	
	Cu(II)	378	1500, 1122	
	I_2 (Vapor)	2954	-	
LDH-Sn_2S_6	ReO_4^{2-}	93	300, 207	[98,102]
MgAl-SnS_4-LDH	Hg(II)	360	-	[115]
SnS_4^{2-}/MgFe-LDH	Hg(II)	342	-	[100]
LDH-Mo_3S_{13}	I_2 (Vapor)	1580	-	[97]
Fe-MgAl-MoS_4-LDH	Se(VI)	167	586, 419	[45]
	Se(IV)	484	1072, 588	

5. Mechanisms for the Removal of Diverse Pollutants by Metal-sulfide/polysulfides LDH

The sorption mechanisms of metal sulfides/polysulfide functionalized LDHs are influenced by various factors. These include the degree of Lewis acidity of the heavy metal cations, the size and charge density of the interlayered anions and their exchangeable counterparts, standard reduction potentials, as well as the type of layered cations and their respective charge densities. The robust chemistry of LDH and their interlayered metals sulfides/polysulfides demonstrate numerous sorption mechanisms including ion exchange, surface sorption, isomorphic substitution, precipitation and adduct formation, and others, as demonstrated in Figure 5. Specific details in some of the notable methods are discussed below.

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5.1. Surface sorption: Surface sorption refers to the adsorption of heavy metals onto the surface of the adsorbent. This process involves the formation of mono and/or multilayers on the sorbent's surface through weak van der Waals forces, without changing their chemical composition on the adsorbent's surface as shown in Figure 5B. Therefore, it exhibits low activation energy, little to no selectivity, and easy adsorption-desorption. The protonated hydroxyl groups ($-OH_2^+$) at the outer surface of the LDH allow it to bind with heavy metal anions through weak electrostatic force. On the other hand, the bare hydroxyl groups on the surface of the LDH can also bind with heavy metal cations through hydrogen bonding.[122]

5.2. Ion exchange: The ion exchange process is the most common phenomenon for the trapping of oxoanionic species in the metal sulfide intercalated LDHs. The Oxoanions of heavy metals and other anions, such as $HAsO_4^{2-}$, $Se^{VI}O_4^{2}$, and others are generally exchanged with the intercalated anions of the LDH layers. The monovalent oxoanions are easily replaceable by the divalent or trivalent metal anion due to the formation of stronger electrostatic forces.[123] However, if the chemical potential of the ion-exchanged LDH is high enough the reverse is also possible. CoAl-MoS_4 showed the anion exchange mechanism for the removal of CrO_4^{2-} anion at acidic, neutral, and basic media.[124] XRD of post-adsorbed studies revealed the increase of basal distance d_{003} at acidic, and neutral media due to the exchange of MoS_4^{2-} by dichromate ($Cr_2O_7^{2-}$) and a mixture of dichromate ($Cr_2O_7^{2-}$) and bichromate ion ($HCr_2O_7^-$), respectively whereas in basic pH the ion-exchange occurs through only chromate anion (CrO_4^{2-}). Similarly, the removal mechanism of rhenium oxoanion, ReO_4^- was also reported as pH dependent. It follows ion exchange in neutral media, however, in acidic solution, it predominantly follows reductive precipitation (soluble $Re^{7+}O_4^- \rightarrow$ insoluble Re(IV). Moreover, the anion-exchange mechanism was also observed for the removal of selenium oxoanions, $Se^{(VI)}O_4^{2-}$ and $Se^{(IV)}O_3^{2-}$ by MgAl-MoS_4-LDH (Figure 5C).[125]

Besides, the heavy metal cation removal process involves interlayered adduct formation into the intercalated metal sulfide anion and the subsequent exchange of this bulky adduct anion with the available NO_3^- or CO_3^{2-} anions in solution.[116] Hence the formation of an adduct and the subsequent ion exchange is related to the concentration of the heavy metals cations in the solutions. For example, as shown in Figure 5A, at extremely low concentrations of the heavy metals cations (M^{n+}), the interlayered metal-sulfide trap M^{n+} and form anionic complexes of $[M_x(MoS_4)_y]^{n-x}$ or $[M_x(Sn_2S_6)_y]^{n-x}$ or $[M_x(Mo_3S_{13})_y]^{n-x}$ and remain inside the LDH layers.[116,122,126] However, with the

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increase of the concentration of M^{n+}, the bulky anions come out from the LDH layers from the interlayer by an exchange with smaller anions, such as nitrate or carbonate anions of the solutions. Hence, depending on the characteristics of the interlayered metal sulfides anion and the pollutant heavy metal cations and its concentration, metal sulfides/polysulfides precipitate out the heavy metal cations either by the formation of charge neutral crystalline metal sulfides or oxides; and amorphous $M^{n+}(M^{II}{}_{x}S_{y})^{n-}$; where M^{n+} = pollutant heavy metals; $(M^{II}{}_{x}S_{y})^{n-}$ = Mo-S or Sn-S anionic species.

Moreover, cations exchange can also occur at the octahedral layers of LDH through the isomorphous exchange.[127] This kind of cation exchange traps the polluted heavy metal cations in the solid state matrix of the LDH layers and thus removes from the solutions. The cationic radii of the heavy metal pollutant and the metal ion forming the LDH sheet play a significant role in the isomorphic ion exchange. For instance, Ni(II) showed the isomorphic ion exchange with Mg(II) in MgAl-LDH since the ionic radii of Ni(II) and Mg(II) are comparable i.e. 70 and 72 pm, respectively.[127]

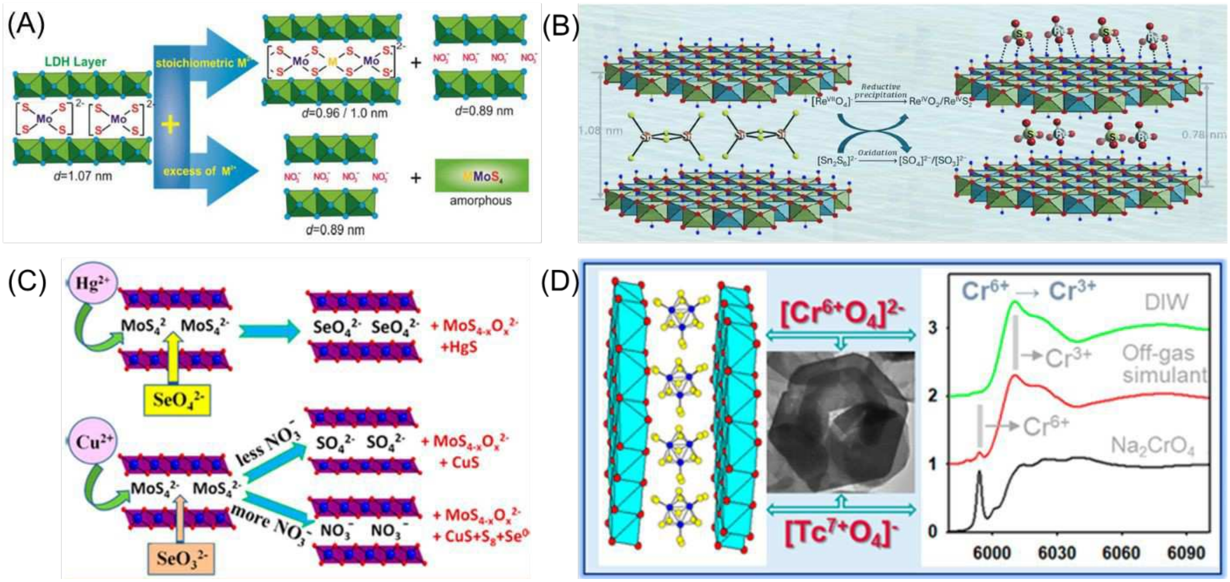

Figure 5: Sorption mechanism of heavy metal ions by metal-sulfide intercalated LDH showing (A) concentration-dependent ion exchange and adduct formation, reprinted with permission From Ma *et al.* [116] copyright 2016 American Chemical Society; (B) Ion exchange, reprinted with permission from Celik *et al.* [122] copyright 2023 American Chemical Society, (C) Reductive precipitation, reprinted with permission from Ma *et al.*[101] copyright 2017 American Chemical Society, and (D) reductive precipitation as well as small contribution of anion exchange and

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5.3. Reductive precipitation: Reductive precipitation is important for the removal of pollutant metal ions and oxyanion species, as the interlayered anionic species of the LDH act as a reductant. For instance, the $Mo^{IV}{}_3S_{13}$ ions of the LDH-$Mo^{IV}{}_3S_{13}$, being disulfide-rich species, reduce Ag^+ ions to metallic Ag^0, facilitating the direct separation of silver from the aqueous solution.[126] In addition, Celik et al. demonstrated that LDH-$Mo^{IV}{}_3S_{13}$ is highly effective in converting highly soluble Cr(VI) ions to insoluble Cr(III) species in aqueous solutions, and in simulated off-gas condensate nuclear waste stream (Figure 5D).[128] This discovery was confirmed through XPS, synchrotron XANES, and EXAFS analyses. However, for the LDH-$Mo^{VI}S_4$, Ma *et al*.[101] reported the reductive precipitation of the Se(IV) ions to Se^0 for the separation of $Se^{IV}O_3{}^{2-}$ in aqueous solutions. Hence, the reduction occurs by the oxidation of sulfides.[125] Overall, the low standard electrode potentials of sulfide $S^{2/1-} \rightarrow S^{n+} + ne^-$ (e.g., E° of $S^{2-}/SO_4{}^{2-}$ is~−0.22) makes it a viable reductant chemically diverse ions.

6. Cost-effectiveness of the metal sulfide/polysulfide intercalated LDHs

LDHs can be synthesized with earth abundance and environmentally benign metal atoms, such as Mg/Al, Ca/Al, using facile, cost-effective, scalable synthesis techniques.[129] Numerous studies suggest the possibility of regeneration, reusing, and high stability of LDHs for absorption applications. This highlights the commercial importance of the LDH as a heavy metal absorbent.[130] Also, sulfur is an environmentally friendly element having an earth abundance of % and is very cost-effective. The metal sulfide anions precursors can be synthesized in solutions and their subsequent intercalation.[131] The metal sulfide anions precursors are commonly prepared by simple cost-effective solution processable hydrothermal method, as well as at room temperature and pressure.[91,102,115,132] Considering these one may surmise that metal sulfide intercalated LDHs will be the economical and efficient candidate for wastewater treatment application.

7. Conclusion and future outlook

Henceforth, polysulfide/metal-sulfide intercalated LDHs exhibit efficacy in the absorption of heavy metal cations and oxoanions of arsenic and selenium from contaminated water. The intercalation of anions leads to an increased interlayer spacing, allowing the formation of

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complexes at the lower concentrations of heavy metals and subsequently being exchanged with the counter anions of the pollutant metal cations at higher concentrations and precipitate out from the solutions. Moreover, sulfide acts as a reductant for the cations having high standard redox potential and separate them from the solution by reductive precipitation. Additionally, the oxoanionic species can be trapped in the interlayer of LDH layers by ion exchange and can be separated from the solutions. These suggest that the sorption process is related to concentration, types of ions, and their redox potential. Therefore, it becomes difficult to make a common judgment about LDH and its efficiency for the environmental remediation of inorganic ions. However, compared with LDH-MoS_4, LDH-Sn_2S_6 offers a higher sorption capacity of Cu, Ag, Pb, Cd, and Hg. Similarly, LDH-Mo_3S_{13} shows higher Ag sorption capacity than LDH-MoS_4. This finding suggests that the sorption capacity of heavy metals may be related to the molar concentration of the active sites, which is sulfide ion in this instant. Despite this observation, one should take a caution to conclude as the actual concentration of sulfide species may be different from their theoretical concentrations in interlayered spaces of the LDH.

While there is substantial progress in the removal of heavy metal ions from solutions, the opportunity remains to investigate their sorption potential for chemically soft noble metal cations. Additionally, the robust chemistry of molecular metal sulfides can extend the chemical compositions of metal sulfide intercalated LDH and their interactions with chemically diverse metal ions. Although the intercalation of bulky metal sulfide into LDH is challenging, a novel synthetic procedure including delamination-restacking or one-pot synthesis techniques may facilitate their intercalation. The challenges in scaling up the preparation of intercalated LDHs lie in the low yield, requiring larger amounts of solvents and intercalating anions. X-ray Diffraction (XRD) studies confirm intercalation by observing shifts in the characteristic peaks of LDHs, yet there is uncertainty regarding structural changes in the metal sulfide anions during the intercalation process. Currently, there is a critical need to develop synthesis methods for metal sulfide intercalated LDHs with high yield, expanding the chemistry of LDH-metal sulfides with chemically diverse metal sulfide anions, overcoming the challenges of regeneration, and demonstrating their practical applications on industrial scales.

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