

Highly Efficient, Rapid, and Concurrent Removal of Toxic Heavy Metals by the Novel 2D Hybrid LDH–[Sn₂S₆]

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ABSTRACT: According to a United Nations’ report, by 2050 nearly six billion people worldwide will suffer from clean water scarcity. This is mostly because of the exponential proliferation of world population, urbanization, industrialization, and water pollution. Heavy metals are common water pollutants that can pose grave public health consequences. Existing water purification systems lack materials that have the potential for quick, simultaneous, efficient, and cost-efficient removal of numerous toxic metals from wastewater. Here, we report the design and synthesis of an economically viable Layered Double Hydroxide - Stannic Sulfide, LDH–[Sn₂S₆] that exhibits a rapid, efficient, selective, and concurrent removal of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ from ppm level to below 5 ppb satisfying World Health Organization’s safe drinking water limit. Moreover, LDH–[Sn₂S₆] shows exceptionally high removal efficiencies of the above metals in acidic, neutral, and basic conditions. LDH–[Sn₂S₆] also demonstrates enormous sorption capacities of 378, 978,

332, 579, and 666 mg/g for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} , respectively. Remarkably, LDH-[Sn_2S_6] displays extraordinary tolerance to the concentrations of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , CO_3^{2-} , NO_3^- , SO_4^{2-} , and other constituents in tap and river water; efficiently sequesters Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} from parts per million (ppm) to safe drinking water levels in minutes. LDH-[Sn_2S_6] shows pseudo-second-order sorption kinetics suggesting chemisorption adsorption mechanism involving M-S bonding. Altogether, the regeneratable LDH-[Sn_2S_6] becomes an exceptional material that shows ultrahigh removal, unprecedented selectivity, rapid adsorption kinetics, wide pH stability, and a massive adsorption capacity. The integration of these features places LDH-[Sn_2S_6] at the top of all adsorbents known to date and thus could be used for wastewater purification.

Keywords:

Heavy metals

Layered double hydroxides (LDHs)

Wastewater treatment

Metal sulfides intercalated LDH

Water purifications

1. Introduction

Worldwide, currently more than one billion people lack access to clean and decontaminated drinking water.^[1, 2] This leads to hundreds of millions of cases of water-related diseases and two to five million casualties each year.^[3, 4] Among the different types of water contaminants, heavy metals pose severe concerns around the world because of their detrimental effects on humans and other biological systems.^[5] The rapid surge of industrialization, urbanization, mining, fossil fuel burning as well as an exponential increase of the use of heavy metals has resulted in their accelerated accumulation in freshwater in recent decades.^[2, 3, 6] Trace heavy metal cations such as mercury, lead, cadmium, silver, and copper commonly play a critical role in the contamination of water.^[7] Decontamination of water from these heavy metal ions is essential because of their severe cytotoxicity to biological systems including human health.^[8, 9] Therefore, over the past decades, an intensive effort has been devoted to the development of techniques and sorbent materials for the remediation of trace heavy metal cations from wastewater.^[6, 10] Among the numerous techniques, physicochemical methods, coagulation and flocculation, electrochemical treatments, bio sorption, membrane filtration, adsorption, chemical precipitation, and ion-exchange are well known.^[7, 8, 10, 11] Despite improvements, efficient removal of heavy metals at trace levels is still the most challenging task.^[7, 8, 11, 12] Chemical precipitation is the broadly applied method for heavy metals removal but the pH needs to be adjusted to perform chemical precipitation.^[13, 14] Ion-exchange can be used for high ion removal efficiency but most of the sorbents possess low selectivity for heavy metal ions.^[10] Chemisorption and physisorption, on the other hand, are considered highly effective and economic methods because of their simple design, high sorption functionality, and low cost.^[15] Numerous adsorbents such as zeolites,^[16] activated carbon^[17], polymers,^[18] biomaterials,^[19] and sorption resins^[20] have been used for the removal of metal ions,

but these materials often show poor selectivity, efficiency, stability, and sorption kinetics. Clays are also considered efficient natural adsorbents because of their low cost, high surface area, and hydrophilicity.^[21] However, they suffer from poor affinity toward trace heavy metals, low selectivity and removal rates, sluggish sorption kinetics, and poor sorption capacity.

Sulfide-based materials show superior affinity toward heavy metal cations and can selectively bind Lewis acidic soft heavy metal ions following Pearson's hard-soft Lewis acid-base principles (HSAB).^[10, 22-25] Thus, this class of materials has emerged as an efficient sorbent for soft heavy metal cations.^[26-28] In recent years, different classes of metal sulfides including layered metal sulfides have been reported as superior sorbents for the removal of soft or relatively soft heavy metal cations. Some examples are: $K_{2x}Mn_xSn_{3-x}S_6$ (KMS-1),^[10, 27, 29, 30] $H_{2x}M_{nx}Sn_{3-x}S_6$ (LHMS-1),^[22, 31, 32] $K_{2x}Mg_xSn_{3-x}S_6$ (KMS-2),^[33, 34] $K_{2x}Sn_{4-x}S_{8-x}$ (KTS-3),^[35] open framework structures such as $K_6Sn[Zn_4Sn_4S_{17}]$ ^[27] and $[(Me)_2NH_2]_2[GeSb_2S_6]$,^[36] porous amorphous glass ($A_2A'_{2-x}SnSb_2S_6$, $A = Na$; $A' = K, Cs$),^[37] chalcogenide-based aerogels,^[38] and metal sulfide-polypyrrole composites.^[39, 40] These materials show selectivity toward heavy metals following the hard-soft Lewis acid-base paradigm.^[24, 25]

Layered double hydroxides (LDHs) are a well-known type of anionic clay that consists of positively charged host layers and ion-exchangeable counter-anions in the interlayers.^[41, 42] This class of clay possesses remarkable intercalation and anion-exchange properties.^[43] These unique features of LDH stimulate us to intercalate them with soft Lewis basic sulfur species such as S_x^{2-} ($x = 2, 4$) and MoS_4^{2-} in the positively charged layers of MgAl-LDH and to study their sorption efficiencies of heavy metal cations.^[41, 44, 45] Given LDHs' attractive 2D structural features, ion-exchange properties, flexibility in the accommodation of inter-layer anions, as well as the demand of ultra-high performing, cost-effective, scalable, high capacity adsorbents of heavy metal cations,

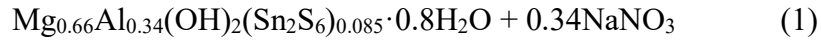
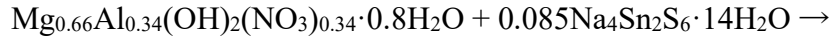
it is tremendously important to explore intercalation chemistry of LDHs with novel soft polarizable thioanions and study their adsorption features of heavy metals.

This study describes the intercalation of $[\text{Sn}_2\text{S}_6]^{4-}$ into the gallery of MgAl—LDH and investigates its effectiveness for the removal of heavy metal ions from aqueous solutions. The as-synthesized hybrid functionalized lamellar MgAl—LDH— $[\text{Sn}_2\text{S}_6]$ (LDH— $[\text{Sn}_2\text{S}_6]$) shows unprecedented removal efficiency of Zn^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} and Hg^{2+} below the WHO limit for drinking water. Its extremely high sorption efficiencies, widespread selectivity, ultrafast sorption kinetics, wide range of pH stability, and reusability place this material at the top of hitherto known sorbents for heavy metals. Thus, this material becomes a promising sorbent for industrial-scale use for the decontamination of heavy metal polluted water.

2. Materials and Methods

2.1 Synthesis: The MgAl—LDH— CO_3 was synthesized according to procedures described in previous work.^[46] In detail, a mixture of 3.21 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0125 mol), 2.34 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.006 mol) and 2.28 g hexamethylenetetramine (HMT) were dissolved in 50 mL deionized water (DIW). Subsequently, the solution was hydrothermally treated at 140 °C for 24 h in a Teflon-autoclave. The as-prepared white precipitate of MgAl— CO_3 —LDH (LDH— CO_3) was filtered, washed with DIW, and then dried under vacuum. MgAl— NO_3 —LDH (LDH— NO_3) was synthesized by the exchange of CO_3^{2-} by NO_3^- , according to the literature.^[46, 47] Specifically, 127.5 g NaNO_3 and 0.36 mL HNO_3 (65%-68%) were dissolved in 1000 mL of DIW and then 0.8 g of MgAl—LDH— CO_3 powder was added. The as-prepared mixture was sealed with Teflon and stirred for 24 h at room temperature. The resulting white solids were filtered, washed with DIW, and then vacuum-dried for 24 h. White crystals of $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ were obtained from a solution

of 14.4 g $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 5.2 g $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ in a refrigerator as previously described.^[48] Crystals of $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ were filtered and washed with acetone and vacuum dried for 24 h. The $[\text{Sn}_2\text{S}_6]^{4-}$ anions of the $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ were exchanged with NO_3^- of the $\text{LDH}-\text{NO}_3$ to synthesize the $\text{LDH}-[\text{Sn}_2\text{S}_6]$ in accordance with equation 1.



For the synthesis of $\text{LDH}-[\text{Sn}_2\text{S}_6]$, typically 0.25 g of $\text{LDH}-\text{NO}_3$ and 0.75 g of $\text{Na}_4\text{Sn}_2\text{S}_6\cdot 14\text{H}_2\text{O}$ were dispersed in 50 mL DIW. The mixture was then stirred at ambient condition for 24 h leading to the formation of a yellowish solution of suspended particles. After filtration, yellow solids were obtained which were then washed with ethanol and dried at room temperature (RT) and pressure.

2.2 Heavy metal uptake experiments

The uptake (e.g., sorption) of heavy metal ions from aqueous solutions of various concentrations of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} were performed at ambient conditions. The sorption experiments were conducted using batch methods where the solid adsorbent, $\text{LDH}-[\text{Sn}_2\text{S}_6]$, was mixed with the solutions of heavy metals for a certain time limit under vigorous stirring. After a certain period of interaction, the suspensions were centrifuged and the supernatant solutions were analyzed for the heavy metals using inductively coupled plasma-mass spectrometry (ICP-MS). The adsorption efficiencies were calculated from the difference in the concentration of the metal cations before and after sorption.

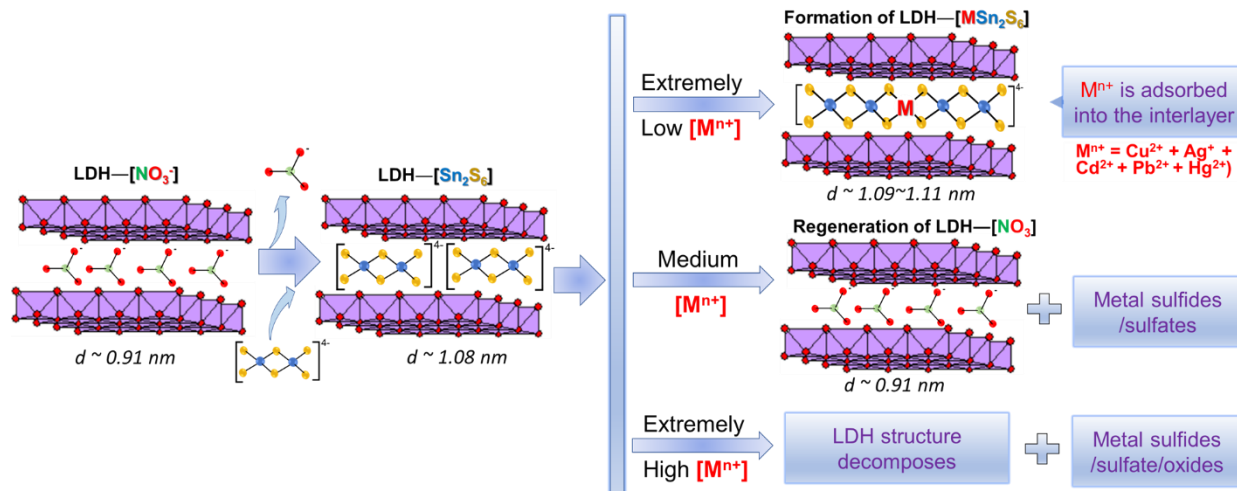
The distribution coefficient (K_d) in adsorption experiments was used to determine the affinity of $\text{LDH}-\text{Sn}_2\text{S}_6$ for heavy metals. The K_d is defined by the equation: $K_d = (V[(C_0 - C_f)/C_f])/m$; where V is the solution volume (mL), C_0 and C_f correspond to the initial and the final

concentrations of the metal cations, M^{n+} ($M^{n+} = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Pb^{2+},$ and Hg^{2+}) in ppm (mg/L), and m is the mass of the solid sorbent (g).^[29] The removal rate of M^{n+} was computed using the equation of $100 \times (C_0 - C_f) / C_0$. The removal capacity, q_m (mg/g) can be obtained from the equation: $10^{-3} \times (C_0 - C_f) V / m$. The adsorption experiments were carried out with $V: m$ ratios of 1000 mL/g, at RT, and at different time scales ranging from min to several h.

3. Results and discussion

3.1 Synthesis and Characterization of the LDH—[Sn₂S₆]

A new hybrid magnesium-aluminum layered double hydroxide, LDH—[Sn₂S₆], was synthesized by the ion-exchange reaction of the NO₃[−] anions in LDH—NO₃ with [Sn₂S₆]^{4−} anions and was investigated for its adsorption characteristics of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ as shown in Schematic 1.



Schematic 1. A schematic of the ion-exchange of NO₃[−] with Sn₂S₆^{4−} anions for the synthesis of LDH—[Sn₂S₆], the proposed concentration-dependent M^{n+} adsorption phenomena leading to the adsorption of M^{n+} into the interlayered gallery, and the regeneration of LDH—NO₃ with settlement of the neutral metal sulfides species outside the LDH gallery.

LDH-[Sn₂S₆] was synthesized at room temperature and pressure and is stable in air and water. To confirm the intercalation of [Sn₂S₆]⁴⁻ anions into the gallery of MgAl-LDH the as-synthesized material was characterized by energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and solid-state UV/Vis optical reflectance. Energy dispersive X-ray spectroscopy shows the presence of Sn and S in addition to Mg and Al in the LDH-Sn₂S₆. An average atomic abundance of Sn and S was determined at 5.17 and 15.90%, respectively, which is equivalent to a Sn:S ratio of 1.0:3.08. This value is close to that expected for Sn₂S₆⁴⁻. Scanning electron microscopic (SEM) observations provide evidence of the retention of the plate like morphology even after the ion-exchange of the LDH—NO₃ with [Sn₂S₆]⁴⁻ (Figure 1). This kind of retention of the morphology after the metal sulfides anion exchange was also observed for polysulfides, S_x and MoS₄²⁻ intercalated LDH.^[44, 45] Elemental mapping shows the homogenous distribution of the Sn and S atoms throughout the hexagonal plates of LDH—[Sn₂S₆], further demonstrating consistent intercalation of [Sn₂S₆] anions (Figures 1D-G).

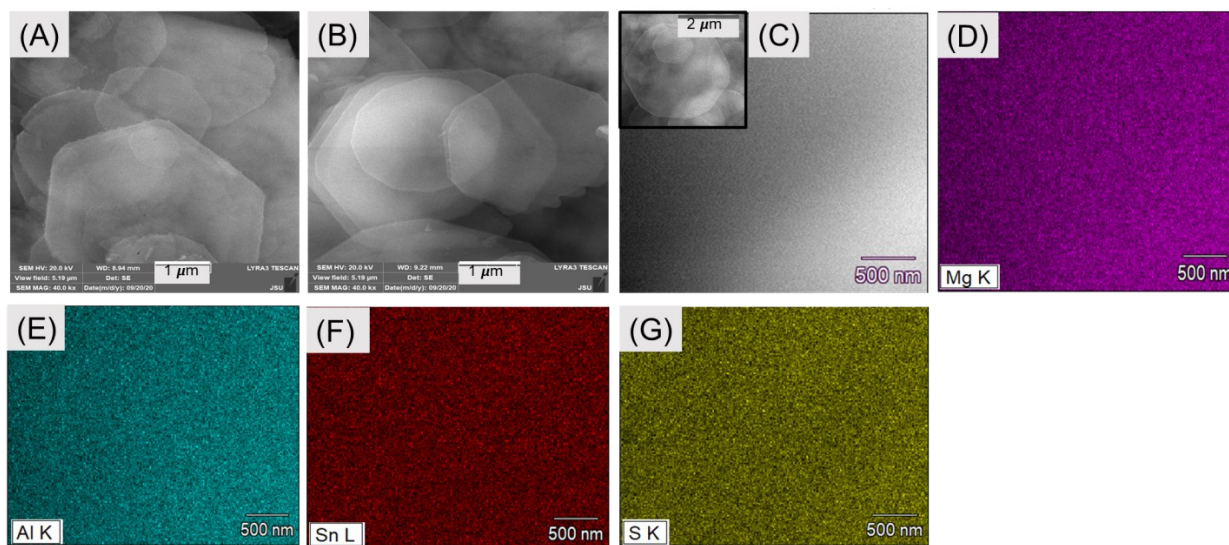


Figure 1. SEM images of the pristine LDH-NO₃ (A) and LDH-[Sn₂S₆] (B) showing well crystalline platelike morphology of the crystallites; section of the hexagonal crystals of LDH-Sn₂S₆ (inset) (C) used for the elemental mapping of Mg, Al, Sn and S (D-G) showing the distributions of Mg, Al, Sn and S.

The evidence of the intercalation of [Sn₂S₆]⁴⁻ into the layers of LDH was further investigated by XRD. A comparable feature of the XRD patterns of CO₃²⁻, NO₃⁻, and [Sn₂S₆]⁴⁻ intercalated LDH is given in Figure 2A. The ion-exchange of CO₃²⁻ by NO₃⁻, and subsequently by [Sn₂S₆]⁴⁻ led to a shift of the LDH's basal spacing (d_{basal}) from 0.74 nm to 0.91 to 1.08 nm, respectively (Figure 2A). Such an increase in the basal spacing is due to the expansion of the unit cell parameter along the 00 l crystallographic plane. Such an enlargement of the unit cell is in agreement with the intercalation of larger [Sn₂S₆]⁴⁻ anions into the LDH. Intercalation of the [Sn₂S₆] into the LDH led to the color change of the samples from white (LDH-NO₃) to yellow (LDH-[Sn₂S₆]). Solid-state optical absorption spectroscopy reveals that LDH-[Sn₂S₆] is a wide band gap semiconductor with an energy of ~3.0 eV (Figure S1, supporting information). The ion-exchange of the nitrate by [Sn₂S₆]⁴⁻ was further confirmed by Raman spectroscopy. A comparable feature of the Raman spectra of Na₄Sn₂S₆, LDH-[NO₃], and LDH-[Sn₂S₆] is presented in Figure S2. For the pristine Na₄Sn₂S₆, a series of vibrational bands were assigned at 163 cm⁻¹ (Na-S), 248 cm⁻¹ (Na-S), 355 cm⁻¹ (Sn-S) with the Sn-S band being the strongest.^[49, 50] For LDH-[Sn₂S₆], a strong band centered at 325 cm⁻¹ is present while this peak is completely absent in the LDH-[NO₃]. This further validates the incorporation of [Sn₂S₆] anions into the LDH. However, a slight shift of the bands can be attributed to the different chemical interactions of Sn₂S₆ anions with positively charged LDH layers. The 1062 and 772 cm⁻¹ bands in LDH-NO₃^[51, 52] are completely absent in the LDH-[Sn₂S₆] demonstrating the complete ion-exchange. In addition, bands at about 180 and 555 cm⁻¹ for the LDH-[NO₃] and LDH-[Sn₂S₆] can be assigned as (M-

O) and (OH—M), respectively.^[53] A small shift in the vibrational energy can be demonstrated as the chemical impact of the different anions.

XPS spectra of the LDH-[Sn₂S₆] revealed the existence of Sn and S with intense bands corresponding to binding energy (BEs) ranges of 157-163 and 482-495 eV, respectively (Figure 2B).^[35, 54, 55] The bands at ~ 485.4 and 493.8 eV are consistent with the 3d_{3/2} and 3d_{5/2} energy levels of Sn⁴⁺.^[35, 55] The splitting of the 3d energy band of Sn⁴⁺ is due to the presence of strong spin-orbital coupling.^[55] In addition, the BE of the bands at 158.2, 159.5, 160.3, and 161.5 eV suggest the presence of S²⁻ ions in the LDH-[Sn₂S₆]. However, the two sets of S²⁻ peaks might be indicative of the different chemical interactions of S²⁻ with the LDH layer hydroxides, probably by Sn—S···HO hydrogen bonding involving the hydroxide ions of the LDH layers.^[35, 54, 56] The binding energies of the Sn 3d and S 2p show the presence of the Sn⁴⁺ and S²⁻ oxidation states of [Sn₂S₆]⁴⁻ confirming its presence in the LDH structure. Photoelectron bands at 89.2 and 74.4 eV for LDH—NO₃ represent Mg 2s and Al 2p, respectively.^[55] In contrast, LDH—Sn₂S₆ displays Mg 2s and Al 2p at 86.6 and 73.4 eV, respectively. Such difference in the binding energies of the Mg 2s and Al 2p can be rationalized by the overall difference in the chemical environment of the NO₃⁻ and Sn₂S₆⁴⁻ intercalated LDH.

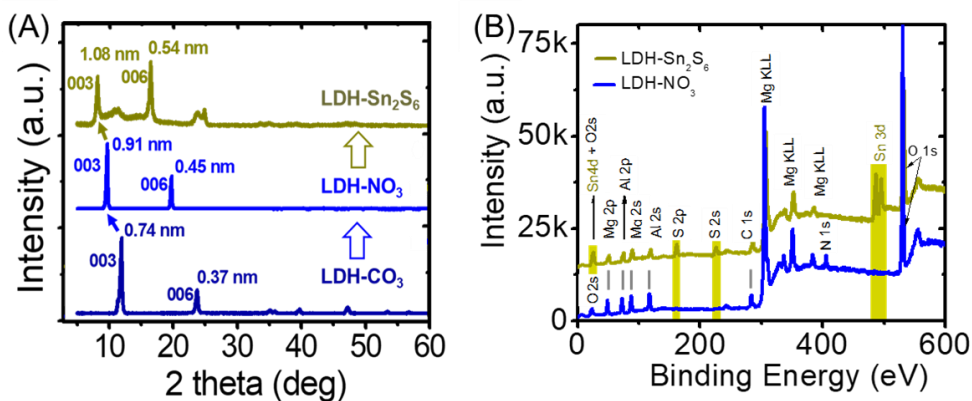


Figure 2. Comparable features of (A) XRD patterns of the LDH-CO₃, LDH-NO₃ and LDH-Sn₂S₆ showing the shift 003 and 006 peaks at lower Bragg angles with respect to the size of

the intercalated anions of CO_3^{2-} , NO_3^- and $\text{Sn}_2\text{S}_6^{4-}$ and (B) XPS of the LDH- NO_3 and LDH- $[\text{Sn}_2\text{S}_6]$ confirm the presence tin and sulfur in the LDH- $[\text{Sn}_2\text{S}_6]$. The XPS peaks were assigned based on the literature.^[55, 57]

3.2 Heavy Metal Removal by LDH- $[\text{Sn}_2\text{S}_6]$

The uptake study of the heavy metal ions ($M^{n+} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+}) was conducted using the batch method at ambient conditions. To determine the affinity of LDH- $[\text{Sn}_2\text{S}_6]$ toward the M^{n+} cations, 10 mg of sorbent material was suspended into the solutions of M^{n+} at different concentrations and pHs and interacted for different time intervals. The supernatant solutions were analyzed by ICP-MS to determine the remaining concentrations of M^{n+} after adsorption by LDH- $[\text{Sn}_2\text{S}_6]$.

At first, the adsorption experiments were conducted with individual solutions of the eight metal ions (Table 1) in DIW. As seen in Table 1, LDH- $[\text{Sn}_2\text{S}_6]$ performed outstandingly for the sorption of Zn^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} from aqueous solutions. The results showed that LDH- Sn_2S_6 can adsorb over 99.9% of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} from 10 ppm (mg/L) solutions of each cation. Such outstanding removal of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} yielded final concentrations of ~ 4 , 1, 1, 2, and 1 ppb, respectively. These metal ion concentrations are well below US EPA and WHO limits for drinking water.^[58-59] Moreover, LDH- $[\text{Sn}_2\text{S}_6]$ exhibits a distribution constant (K_d) of $\sim 10^4$ mL/g for Zn^{2+} and $>10^6$ mL/g for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} . It is important to note that K_d represents the affinity of a sorbent toward a species and a value of $\geq 10^4$ mL/g is considered outstanding.^[35, 53, 60] Hence, LDH- $[\text{Sn}_2\text{S}_6]$ with such an excellent removal capacity, unprecedented selectivity toward a large number cations (Zn^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+}) and outstanding K_d place this material as the topmost candidate for the sorption of heavy metals from aqueous solutions.

Table 1: Results from adsorption studies of LDH- $[\text{Sn}_2\text{S}_6]$ with eight individual heavy metal cations (initial concentration: 10 ppm^{a,b} in DIW).

Single ions	C _i (ppm)	C _f (ppm)	M ⁿ⁺ removal %	K _d (mL/g)
Co ²⁺	10	9.5	5.00	5.26 × 10 ¹
Ni ²⁺	10	9.4	6.00	6.38 × 10 ¹
Zn ²⁺	10	0.62	93.80	1.51 × 10 ⁴
Cu ²⁺	10	0.004	99.96	2.50 × 10 ⁶
Ag ⁺	10	0.001	99.99	1.0 × 10 ⁷
Cd ²⁺	10	0.001	99.99	1.0 × 10 ⁷
Pb ²⁺	10	0.002	99.98	5.0 × 10 ⁶
Hg ²⁺	10	0.001	99.99	1.0 × 10 ⁷

^aion concentration: ~10 ppm per ion. Contact time: 3h; ^bV=10 mL; mass of solid sample = 0.010 g; V/m ratio =1000 mL/g and pH~7. C_i = initial (pre-adsorption) concentration, C_f = final (post adsorption) concentration.

To determine the selective affinity and the competitive sorption of trace heavy metal cations, 10 mg of LDH-[Sn₂S₆] sorbents were suspended into a solution that contained Mⁿ⁺ = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ together, a solution that we call mixed-ion states (Table 2). A solution of 10 ppm for each of eight cations results in a total concentration of 80 ppm. The sorption experiment was conducted at pH ~7 for a contact time of 3h. Remarkably, even in the presence of mixed-competing ions, the affinity and the removal capacity of the sorbent was as high as for the individual cations Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ with the final concentrations of these cations as low as 5 ppb. More precisely, the removal capacity in the mixed-ion states is over 99.9% and K_d values reach ~10⁶ mL/g for Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺ and Hg²⁺. At these concentrations, the selectivity order for these ions was Zn²⁺, Co²⁺, Ni²⁺<< Ag⁺, Cu²⁺< Hg²⁺< Pb²⁺, Cd²⁺. The concurrent removal of such a large number of heavy metals ions (Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺), excellent K_d values, and ultrahigh removal capacity for a single adsorbent is yet to be known in the literature. A comparison of the adsorption data for the individual and mixed cation experiments demonstrates that at neutral pH, LDH-Sn₂S₆ is similarly effective in both systems for Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺. However, our results show the adsorption of Zn²⁺ dropped from ~ 94% (K_d ~ 1.5×10⁴) to ~ 6% (5.5×10¹ mL/g) from the individual to mixed cations systems. This finding suggests that the Zn²⁺ cations are less selective for the LDH-Sn₂S₆. This could be due to its higher

chemical hardness and thus lower affinity for the chemically soft and polarizable sulfide anions. Overall, a combination of such outstanding sorption efficiencies establishes LDH-[Sn₂S₆] as a highly promising adsorbent for the removal of heavy metals from complex samples and wastewater treatment that we have discussed in more detail in section 4.

Table 2. Adsorption studies of LDH-[Sn₂S₆] toward mixed-eight ions with 10 ppm concentrations for each cations meaning 80 ppm all together in DIW.

Mixed-ions	C _i (ppm)	C _f (ppm)	M ⁿ⁺ removal (%)	K _d (mL/g)
Co ²⁺	10	9.91	0.90	0.91 × 10 ²
Ni ²⁺	10	9.90	1.00	1.01 × 10 ¹
Zn ²⁺	10	9.45	5.50	5.82 × 10 ¹
Cu ²⁺	10	0.005	99.95	2.00 × 10 ⁶
Ag ⁺	10	0.005	99.95	2.00 × 10 ⁶
Cd ²⁺	10	0.001	99.99	1.00 × 10 ⁷
Pb ²⁺	10	0.001	99.99	1.00 × 10 ⁷
Hg ²⁺	10	0.004	99.96	2.50 × 10 ⁶

contact time: 3h; V=10 mL; *m* (mass of solid sample) = 0.010g; V/*m* ratio = 1000 mL/g; and pH: 7. C_i= initial (pre-adsorption) concentration, C_f= final (post adsorption) concentration.

LDH-[Sn₂S₆] was also studied at pH ranging from 2 to 12 to determine the stability as well as the sorption efficiencies for Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ ions (Table S1). This experiment was conducted by 3 h interactions between cation solutions sorbents. Strikingly, our study revealed that LDH-[Sn₂S₆] could efficiently capture these cations within this pH range (Figure 3).

A detailed analysis of the pH dependent study shows that LDH-Sn₂S₆ is the most efficient at adsorption of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ ions at pH~7. At this pH, it achieves ≥ 99.9% removal of each cation with K_d values >10⁶ mL/g. At pH ~2, K_d values for Cu²⁺, Ag⁺, and Pb²⁺ decrease about one order of magnitude and their removal rates decrease to 99.7, 99.5, and 99.0%, respectively. In contrast, K_d values remain >10⁷ mL/g for Hg²⁺ in the pH range of 2 to 7. Remarkably, the K_d and removal rate for Cd²⁺ remain at ~10⁶ mL/g and >99.9%, respectively, over the pH range of ~2 to 12. At pH ~12, we observed similar results for the absorption of Cu²⁺ and Ag⁺ (~99.0%, K_d~10⁵ mL/g). On the contrary, the removal of Hg²⁺ remains over 99.9 % in the pH

range of two to nine but decreases to ~72 % at pH ~12. The removal of Pb^{2+} varies from 99% ($K_d \sim 10^5$ mL/g) at pH ~2 to about 33% ($K_d \sim 5.2 \times 10^2$ mL/g) at pH ~12. The decreased removal efficiencies of Pb^{2+} and Hg^{2+} at higher pH can be related to the gradual hydrolysis of the LDH. In contrast, the higher removal of Cu^{2+} , Ag^+ , and Cd^{2+} at pH ~12 could be a co-operative effect of both the adsorption and metal hydroxide precipitation. These high removal capacities and remarkably high distribution constants reveal LDH-[Sn_2S_6] as an unprecedented sorbent for the adsorption of heavy metals ions from acidic, alkaline, and neutral wastewater.

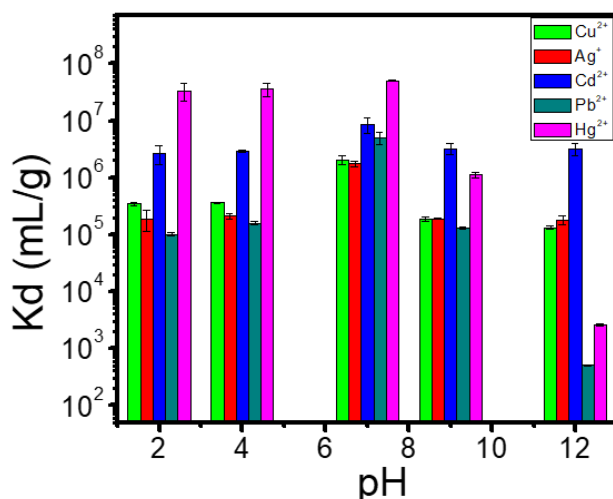


Figure 3: Distribution constants, K_d versus pH show the excellent sorption efficiencies of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} in acidic, alkaline, and neutral media.

3.3 Adsorption Kinetic Studies of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+}

The kinetics for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} adsorption by LDH-[Sn_2S_6] were studied to determine adsorption rates and understand the adsorption mechanism until it reaches equilibrium. In general, the adsorption rate is determined by two different rate equations, known as pseudo-first-order and pseudo-second-order mechanisms. Here, we used these mechanisms to analyze the adsorption phenomena of the LDH-[Sn_2S_6]. The comparison was then drawn between the experimental and calculated data. The two kinetic rate equations are as follows:^[61]

Pseudo-first-order:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where, q_e (mg/g) is the amount of adsorbed element per unit mass of adsorbent 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 rate constants of pseudo-first-order and pseudo-second-order adsorption interactions, respectively.^[62] 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 (Figure 4).

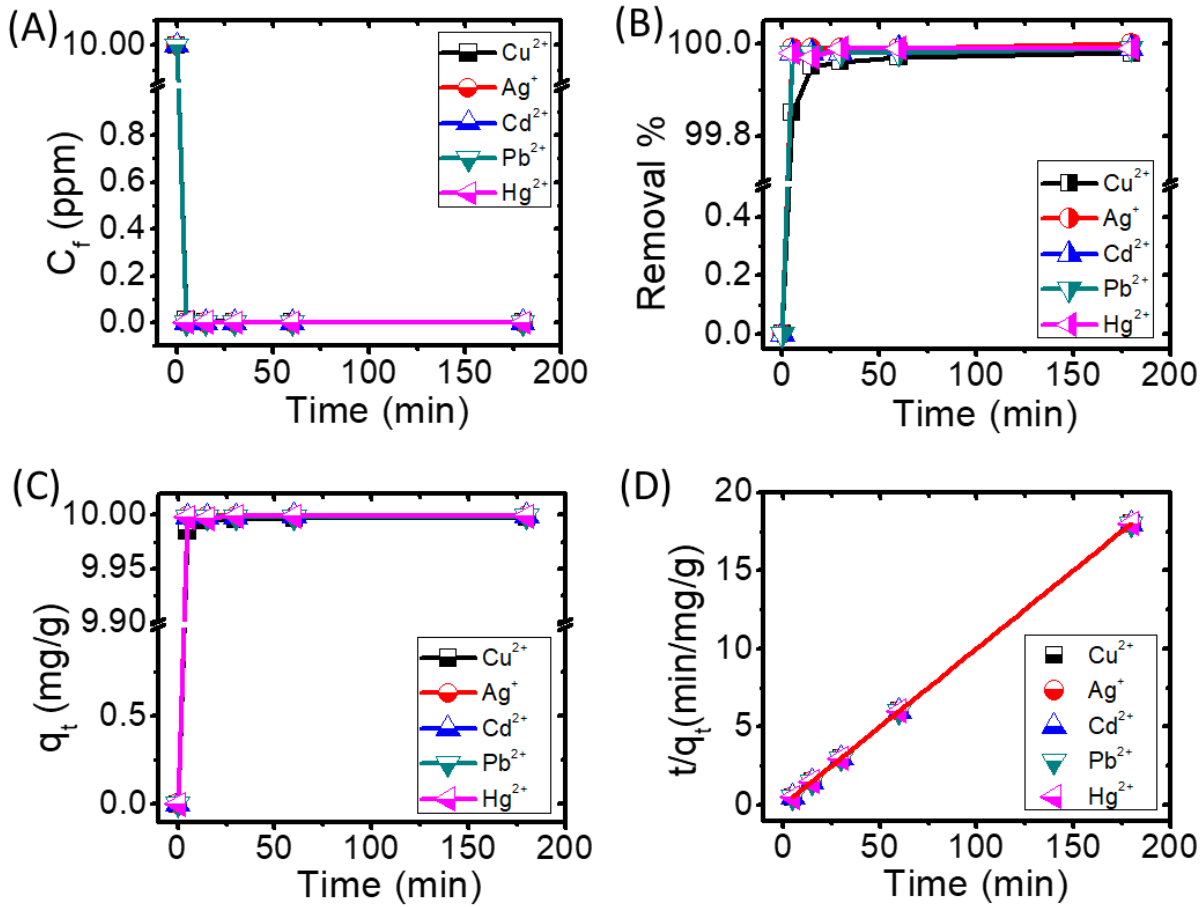


Figure 4. Adsorption kinetics curves for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} ; (A) Ion concentration change with contact time, (B) Removal % as a function of contact time, (C) Sorption capacity(q_t) with contact time, and (D) pseudo-second-order kinetic plots.

As shown in Figure 4 and in Table S2, the adsorption rates for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} ions in the DIW for 10 ppm of concentrations of each cation are extremely rapid. Within only 5 min, the LDH-[Sn_2S_6] achieved ~ 99.9 % removal of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} with K_d values of over 10^5 mL/g for each cation. The removal capacity and K_d reached virtually ~100% and $>10^6$ mL/g, respectively, for all five cations within 1h. Overall, these experiments revealed that the adsorption for all five cations reaches equilibrium just in 5 min. A similar trend in the adsorption kinetics was observed for Hg^{2+} by LDH-MoS₄,^[45] and for Hg^{2+} , Ag^+ , and Pb^{2+} by polypyrrole-MoS₄.^[40] But to the best of our knowledge, such a rapid and efficient removal for a large number of cations, Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} down to trace levels by a single adsorbent has not been reported in the literature.

A plot of t/q_t against t showed a linear relationship for all five cations (Figure 4D). The kinetic parameters for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} are summarized in Table S3. The calculated sorption capacities ($q_{e,\text{cal}}$) derived from pseudo-second-order model are close to corresponding experimental values ($q_{e,\text{exp}}$). The goodness of fit parameter (R^2), is close to unity for all the cations. This indicates that adsorption for these ions onto LDH-[Sn_2S_6] follows pseudo-second-order kinetics, suggesting that the adsorption follows chemisorption pathways.^[63]

3.4 Adsorption isotherms and the uptake capacity for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+}

As shown in the above results, LDH-[Sn_2S_6] exhibits high affinity to capture Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} . To determine the maximum sorption capacity of LDH-[Sn_2S_6] for these

cations, an adsorption equilibrium study was carried out over a concentration ranging from 10 to 1500 ppm (Table S4). This study revealed increasing adsorption with the increasing concentrations of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} (Figures 5 and S3) before reaching equilibrium.

LDH-[Sn_2S_6] achieved the maximum adsorption capacity of 378 mg/g for Cu^{2+} (Figure S3, Table S4). With this high absorption capacity, LDH-[Sn_2S_6] outperforms the high performing adsorbents known to date.^[44,45, 64-70] As an example, the adsorption capacity for Cu^{2+} is much higher than highly performing sorbents, namely MoS_4 -LDH (181 mg/g),^[45] PANI-PS (171 mg/g),^[69] KMS-1 (156 mg/g),^[70] S_x -LDH (127 mg/g),^[44] and others (Table 3).

More strikingly, the LDH-[Sn_2S_6] exhibits ultra-high removal of Ag^+ over a wide range of initial concentrations (10 to 300 ppm). For the entire concentration range, the sorption of Ag^+ remains over 99.9% with K_d^{Ag} values of over 10^5 mL/g (Table S4). The maximum adsorption capacity (q_m^{Ag}) reached a value of 978 mg/g (Figure S3, Table S4). As seen in Table 3, this value is exceptionally high when compared to other top materials such as Ni/Fe/Ti- MoS_4 -LDH (856 mg/g),^[71] Mn- MoS_4 (564 mg/g),^[72] MoS_4 -LDH (550 mg/g),^[45] MoS_4 -ppy (480 mg/g at pH ~5),^[40] and Mo_3S_{13} -Ppy (408 mg/g).^[39]

Over 99% of Cd^{2+} was removed for concentrations up to 50 ppm with K_d^{Cd} values in the range of $\sim 10^4$ to $\sim 10^6$ mL/g. The maximum adsorption capacity obtained was 332 mg/g, which is higher than any of the high performing Cd^{2+} adsorbents listed Table 3 and comparable to KTS-3.^[35] A similar removal rate (99.9%) was found for Pb^{2+} for concentrations up to 50 ppm. The maximum capture capacity achieved for Pb^{2+} (579 mg/g) was recorded for a 1500 ppm spiked solution. To the best of our knowledge this places LDH-[Sn_2S_6] at the top of all the high performing Pb^{2+} adsorbents (Table 3).

We have also investigated the adsorption capacity of Hg^{2+} for a solution of 10 to 1500 ppm. Importantly, LDH-[Sn_2S_6] can remove $\geq 99.9\%$ of Hg^{2+} from a 500 ppm solution (Table S4). At concentrations from 10 to 500 ppm, the K_d^{Hg} values remain in the range of 10^5 - 10^6 mL/g. The maximum Hg^{2+} removal capacity of ~ 666 mg/g is higher than any known adsorbents (Table 3). The outcome of this study suggests that LDH-[Sn_2S_6] is a unique adsorbent that outperforms for the sorption of a large number of heavy metals cations as discussed above (Table 3).

As seen in Table 3, metal sulfide or polysulfide intercalated LDHs, such as LDH- MoS_4 and LDH- S_x ($x = 2-4$) are highly efficient for the adsorption of heavy metal cations.^[44, 45] The novel LDH- Sn_2S_6 is a new member of this family. As discussed above, the adsorption phenomena of heavy metals by the metal sulfides or polysulfides intercalated LDHs are mainly governed by the covalent interactions of the Lewis basic sulfide anions and the Lewis acidic soft heavy metal cations following the Hard-soft Lewis Acid-base paradigm^[24, 25, 44, 45] Additionally, this class of materials involves numerous M^{n+} adsorption mechanisms, such as adduct formation in the interlayer spaces, metal-sulfide covalent interactions, and cation-exchange in the positively charged layers of the LDHs. Overall an integration of strong affinity of the sulfide species and numerous additional adsorption mechanisms makes metal sulfide or polysulfide intercalated LDHs superior adsorbents of heavy metals. Among the metal sulfide or polysulfide intercalated LDHs, LDH- Sn_2S_6 exhibits the largest interlayer spacing that could facilitates the facile diffusion of cations into the interlayer spaces. However, the role of the host-guest interactions, relative interactions of M-S for MoS_4 and Sn_2S_6 anions, and surface modifications for the adsorption of heavy metals by different metal sulfides/polysulfide intercalated LDHs cannot be ruled out. Overall, this study revealed that such tremendously higher adsorption capacities of such a large range of cations by a single adsorbent is not known to the best of our knowledge.

Table 3. Comparison of adsorption capacities for heavy metals with the known high performing sorbents

Cations	Adsorbents	q _m (mg/g)	References and Journal name
Cu²⁺	LDH-[Sn ₂ S ₆]	378	This work
	MoS ₄ -LDH	181	[45] <i>J. Am. Chem. Soc.</i> 2016
	PEI-modified biomass	92	[64] <i>Environ. Sci. Technol.</i> 2005
	TA-HTC	81	[65] <i>Appl. Clay Sci.</i> 2008
	H100-LDH	85	[66] <i>Chem. Eng. J.</i> 2015
	EDTA-LDH	71	[67] <i>Chem. Eng.</i> 2016
	Fe-MoS ₄	117	[68] <i>ACS Appl. Mater. Interfaces</i> 2017
	Sx-LDH	127	[44] <i>J. Mat. Chem.</i> 2014
	PANI-PS	171	[69] <i>ACS Appl. Mater. Interfaces</i> 2015
	KMS-1	156	[70] <i>J. Mol. Liq.</i> 2014
Ag⁺	LDH-[Sn ₂ S ₆]	978	This work
	Mo ₃ S ₁₃ -ppy	408	[39] <i>J. Am. Chem. Soc.</i> 2020
	Ni/Fe/Ti-MoS ₄ -LDH	856	[71] <i>RSC Adv.</i> 2020
	Mn-MoS ₄	564	[72] <i>Chem. Eng. J.</i> 2018
	MoS ₄ -Ppy	480 (pH ≈ 5) 725 (pH ≈ 1)	[40] <i>Adv. Funct. Mater.</i> 2018
	MoS ₄ -LDH	450	[45] <i>J. Am. Chem. Soc.</i> 2016
	Sx-LDH	383	[44] <i>J. Mat. Chem. A</i> 2014
	KMS-2	408	[33] <i>Chem. Mater.</i> 2015
	Fe-MoS ₄	565	[68] <i>ACS Appl. Mater. Interfaces</i> 2017
Cd²⁺	LDH-[Sn ₂ S ₆]	332	This work
	DPA-LDH	258	[73] <i>Chem. Eng. J.</i> 2017
	Biomass based hydrogel	161	[74] <i>Sci. Rep.</i> 2020
	NH ₂ -Functionalized Zr-MOFs	177	[75] <i>Ind. Eng. Chem. Res.</i> 2017
	Polysulfide-LDH	57	[44] <i>J. Mat. Chem.</i> 2014
Pb²⁺	LDH-[Sn ₂ S ₆]	579	This work
	MOF/polydopamine	394	[76] <i>ACS Cent. Sci.</i> 2018
	MoS ₄ -LDH	290	[45] <i>J. Am. Chem. Soc.</i> 2016
	Mn-MoS ₄	357	[72] <i>Chem. Eng J.</i> 2018
	Fe-MoS ₄	345	[68] <i>ACS Appl. Mater. Interfaces</i> 2017
	EDTA-LDH	180	[77] <i>Chem. Lett.</i> 2004

	Cellulose based charcogel	240	[78] <i>ACS Appl. Mater. Interfaces</i> 2015
	Biomass based hydrogel	422.7	[74] <i>Sci. Rep.</i> 2020
Hg²⁺	LDH-[Sn₂S₆]	666	This work
	MoS ₄ -LDH	500	[45] <i>J. Am. Chem. Soc.</i> 2016
	Mn- MoS ₄	594	[72] <i>Chem. Eng. J.</i> 2018
	Fe-MoS ₄	582	[68] <i>ACS Appl. Mater. Interfaces</i> 2017
	MOF/PDA	1634	[76] <i>ACS Cent. Sci.</i> 2018
	KMS-2	297	[33] <i>Chem. Mater.</i> 2015
	MoS ₄ -Ppy	210	[39] <i>Adv. Funct. Mater.</i> 2018
	KMS-1	377	[32] <i>Adv. Funct. Mater.</i> 2009

We used the Langmuir isotherm to model experimentally obtained adsorption data. This model predicts that adsorbate moieties undergo monolayer type coverage on the surface of the adsorbent. It assumes that once an adsorption site is occupied, no further adsorption can occur at the same site. The Langmuir isotherm model is shown as equation (4):

$$q = q_m \frac{bC_e}{1+bC_e} \quad (4)$$

where C_e (mg/L) is the concentration at equilibrium, q (mg/g) is the equilibrium sorption capacity of the adsorbed M^{n+} (Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+}), q_m (mg/g) is the theoretical maximum sorption capacity, b ($L \cdot mg^{-1}$) is the Langmuir constant, and C_e (mg/L) is the equilibrium concentration. The equilibrium adsorption isotherms for Cd^{2+} , Pb^{2+} , and Hg^{2+} are shown in Figure 5. The experimentally obtained data for the adsorption of each cation are fitted with the Langmuir model. The correlation coefficient, R^2 was ≥ 0.98 for Cu^{2+} , 0.93 for Ag^+ , 0.98 for Hg^{2+} , 0.95 for Cd^{2+} , and 0.98 for Pb^{2+} suggesting a good fit with the Langmuir model (Figures 5 and S3).

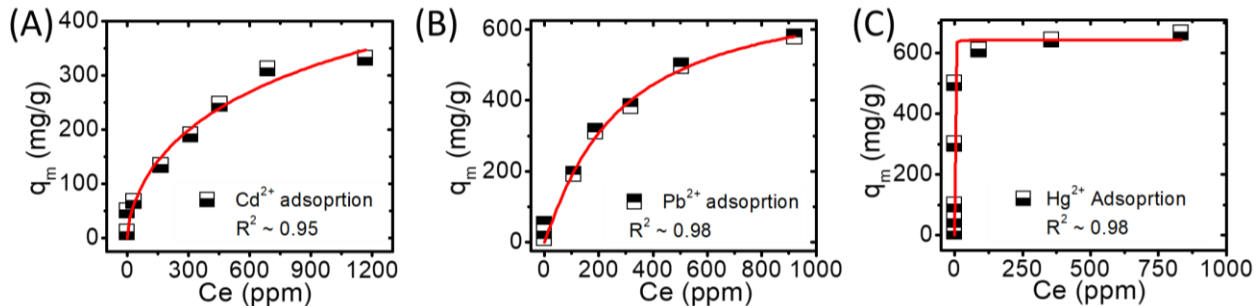


Figure 5: Sorption isotherms of Cd^{2+} (A), Pb^{2+} (B), and Hg^{2+} (C) at $\text{pH} \sim 7$, derived from the experimental data fitted with Langmuir model at equilibrium concentrations (C_e) and adsorption capacity (q_m).

Considering the anion, $[\text{Sn}_2\text{S}_6]^{4-}$ as the adsorption site for the capture of heavy metal ions, one can determine the theoretical maximum adsorption capacity based on the content of $[\text{Sn}_2\text{S}_6]^{4-}$ in the LDH. The molecular weight of LDH- $[\text{Sn}_2\text{S}_6]$ is 110 g based on its chemical formula $\text{Mg}_{0.66}\text{Al}_{0.34}(\text{OH})_2(\text{Sn}_2\text{S}_6)_{0.085} \cdot 0.8\text{H}_2\text{O}$ with a contribution from the Sn_2S_6 moiety of 36.53 g/mol. Therefore, 1 g of LDH- $[\text{Sn}_2\text{S}_6]$ contains 7.7×10^{-4} mol ($1 \text{ g} \times 0.085 \text{ mol} / 110 \text{ g}$) of $[\text{Sn}_2\text{S}_6]^{4-}$. In parallel to LDH- MoS_4 ,^[45] the adsorption mechanisms for LDH- $[\text{Sn}_2\text{S}_6]$ is assumed as the binding of M^{n+} cations with $[\text{Sn}_2\text{S}_6]^{4-}$ toward the formation of an adduct. Consequently, in the case of Ag^+ sorption, one mol of $[\text{Sn}_2\text{S}_6]^{4-}$ will bind with maximum 4 mol of Ag^+ to yield a theoretical maximum sorption capacity of Ag^+ is 333 mg ($= 7.7 \times 10^{-4} \text{ mol} \times 4 \times 108 \text{ g/mol} \times 10^3 \text{ mg}$). Similarly, the theoretical maximum adsorption capacity for the divalent cations ($2\text{M}^{2+}:[\text{Sn}_2\text{S}_6]^{4-}$) is 98 mg for Cu^{2+} , 173 mg for Cd^{2+} , 308 mg for Hg^{2+} , and 319 mg for Pb^{2+} . In contrast, the maximum experimental sorption capacities were obtained as 378 mg for Cu^{2+} , 978 mg for Ag^+ , 332 mg for Cd^{2+} , 579 mg for Pb^{2+} , and 666 mg for Hg^{2+} (Tables 3 and S4). Here, the experimental adsorption capacity for each cation is substantially larger than the value determined based-on the above-mentioned binding mechanism of charge balance. This suggests that the adsorption mechanism is more complex, and may involve different or multiple mechanisms.

At this stage, we consider each sulfide (S^{2-}) of the $[Sn_2S_6]^{4-}$ as an active site for covalent bonding interactions with M^{n+} to form M–S chemical bonding. There are 4.6×10^{-3} moles of S in 1 g of $Mg_{0.66}Al_{0.34}(OH)_2(Sn_2S_6)_{0.085} \cdot 0.8H_2O$. Based on M–S covalent bonding, $M^{2+}: S^{2-} = 1:1$ ($M^{2+} = Cu^{2+}, Cd^{2+}, Pb^{2+}$ and Hg^{2+}) and $M^+: S^{2-} = 2:1$ ($M^+ = Ag^+$), one can determine the theoretical saturation limit for the adsorption capacity. Therefore, the theoretical maximum sorption capacity of Ag^+ for the covalent bonding mechanism is 994 mg/g ($= 4.6 \times 10^{-3} \text{ mol} \times 2 \times 108 \text{ g/mol} \times 10^3 \text{ mg}$). Similarly, the maximum theoretical adsorption capacity for Cu^{2+} , Cd^{2+} , Pb^{2+} , and Hg^{2+} is 292, 517, 952, and 920 mg/g, respectively. The similarity between the covalent bonding theoretical sorption capacity for Ag^+ (994 mg/g) and the experimental capacity (978 mg/g) suggests the validity of this mechanism. The formation of Ag_2S and $AgSO_4$ in the final products of the adsorbed samples further validates this binding mechanism. For Cu^{2+} , the experimental adsorption capability of 378 mg/g surpasses the theoretical capacity of 292 mg/g. This additional adsorption could be attributed to the incorporation of Cu^{2+} in the Mg/Al octahedral sites of the LDH layers by substitution. Hence, higher concentration of Cu^{2+} may facilitate the substitution of Cu^{2+} by Mg^{2+} . This kind of phenomenon was reported for $K_{2x}Mg_xSn_{3-x}S_6$ ($x = 0.5-1$).^[33, 34] On the other hand, experimental adsorption capacities for Cd^{2+} , Hg^{2+} , and Pb^{2+} satisfy none of the mechanisms alone. Since the experimental sorption capacities remain somewhere in between mechanism $M^{n+}/[Sn_2S_6]^{4-}$ adducts formation and $M^{n+}-S^{2-}$ covalent bonding, one can assume a combination of the mechanisms. The possibility of the partial substitution of layered Mg^{2+} by M^{n+} , especially by Cd^{2+} as we discussed above for Cu^{2+} cations, cannot be ruled out. Overall, the different adsorption phenomena of the 2D Hybrid LDH- $[Sn_2S_6]$ for heavy metals can be demonstrated by hard-soft Lewis acid base (HSAB) principle.^[24, 25] In accordance with this principle, chemically soft and polarizable Lewis basic sulfide anions will preferentially bind with soft Lewis acidic heavy metal

cations. Hence, the degree of the M-S bonding interactions depends on the relative chemical hardness of cations. Apart from this, the adsorption of transition metals, such as Cu^{2+} and Cd^{2+} , especially at higher concentrations, can be achieved by the exchange with Mg^{2+} cations of the positively charged layer of $[\text{Mg}_x\text{Al}_{1-x}\text{O}_6]$ octahedra. Here the cation-exchange could be facilitated by the relatively preferred coordination preferences to the octahedral geometry of the $[\text{Mg}_x\text{Al}_{1-x}\text{O}_6]$ (e.g., oxides) layer of LHD.

3.5 Morphology and structural characterization of post-adsorption solid samples

To understand the structure, morphology, and physicochemical interactions of the sorbents toward the heavy metal cations, the solid sorbents were collected after the sorption experiments, dried, and analyzed by SEM-EDS, XRD, and XPS.

SEM images show that retention of the platelike hexagonal morphology of the LDH- $[\text{Sn}_2\text{S}_6]$ crystallites is related to the concentrations of the M^{n+} . For example, after treating the samples at concentrations of 10 and 100 ppm, the adsorbates seem to maintain the platelike morphology (Figure 6) indicating that the layered structure still dominates after cation sorption. A similar phenomenon was also observed in other intercalated LDH during adsorption of heavy metal cations.^[41, 44, 45] In contrast, at extremely high concentrations of M^{n+} , here in the case of 1500 ppm, the platelike morphology of the LDH- Sn_2S_6 is absent. Instead, we can see the formation of aggregated nanoparticles. EDS analyses of LDH- Sn_2S_6 treated with M^{n+} show that the quantity of the metal cation increases with the increase of the initial concentrations of the respective metal ions (Table S5-9). This finding is in agreement with the increased adsorption of M^{n+} cations with the higher initial concentrations as discussed above.

The adsorption of M^{n+} was achieved at different concentrations in the range of 100 ppb to 1500 ppm. At extremely low concentration (~ 100 ppb) the basal space of post-adsorbed LDH- $[\text{Sn}_2\text{S}_6]$

expands from 1.08 to 1.10 nm for Pb^{2+} and Cd^{2+} and to 1.09 nm for Ag^+ , Cu^{2+} and Hg^{2+} . This suggests that, at such an extremely low concentration, the interlayer $\text{Sn}_2\text{S}_6^{4-}$ anions holds the M^{n+} cations and the structure of LDH- $[\text{Sn}_2\text{S}_6]$ dominates. A similar observation was reported for the polysulfide and MoS_4^{2-} intercalated LDHs.^[44, 45] However, at 10 ppm of the M^{n+} solutions, the (003) Bragg peak shifts from 1.08 to ~ 0.91 nm which is equivalent to that of the LDH- NO_3 . It suggests that, at this concentration, the LDH- NO_3 regenerates by the exchange of Sn_2S_6 anions. The nitrate anions are present in solution as the anion of the M^{n+} salts used adsorption study. The presence of the (00 l) peaks in the XRD diffraction patterns of the 100 ppm M^{n+} adsorbed samples shows that they keep the nitrate intercalated LDH structure (Figure S4). SEM images confirm the retention of the hexagonal morphology of the crystallites at these concentrations. XRD patterns of the M^{n+} adsorbed samples at concentrations ≥ 1000 ppm show the absence of the layered structures of LDH. This suggests that the LDH structure does not sustain at such extremely high metal concentrations.

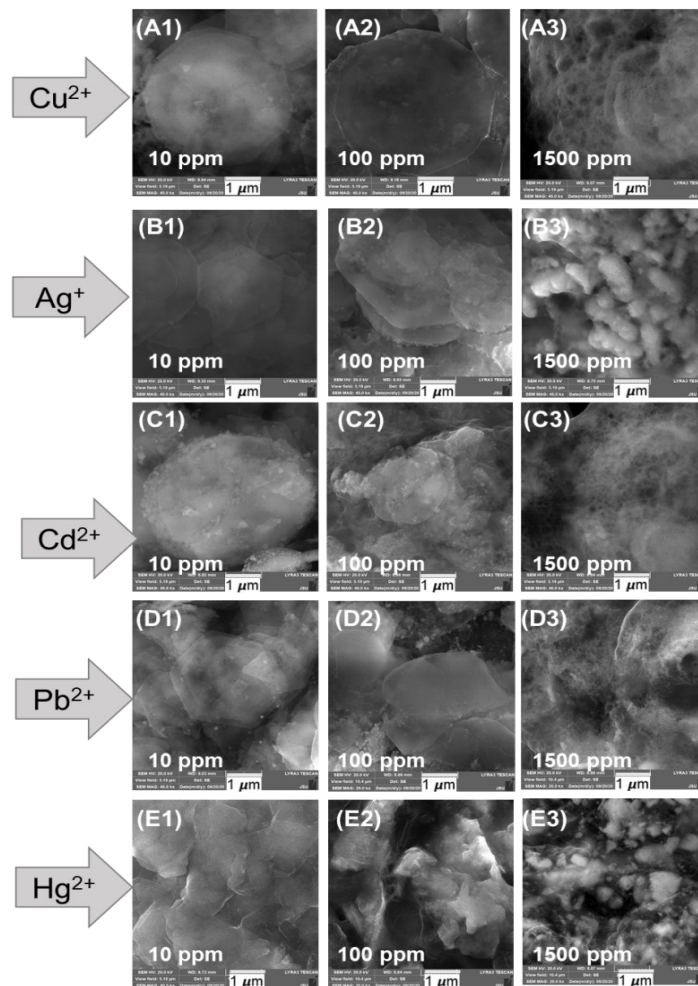


Figure 6. Scanning electron microscopy images of LDH-[Sn₂S₆], after the adsorption of 10, 100 and 1500 pm of Cu²⁺ (A1, A2 and A3); Ag⁺ (B1, B2, B3); Cd²⁺ (C1, C2, C3); Pb²⁺ (D1, D2, D3), and Hg²⁺ (E1, E2, E3) demonstrating change in the morphology with the concentrations of heavy metal ions.

X-ray photoelectron spectroscopy (XPS) was conducted to determine the surface compositions and the chemical states of the post-adsorbed samples from 100 ppm solutions of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ (Figure 7). XPS of the Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ adsorbed samples show the presence of these metals. For the Cu²⁺ adsorbed sample (Figure 7C), the bands centered at 932.3 and 952.5 eV correspond to the Cu 2p energy of the LDH-[Sn₂S₆].^[55, 79] For the Ag⁺ adsorbed sample, two bands centered at 368.2 and 374.11 eV can

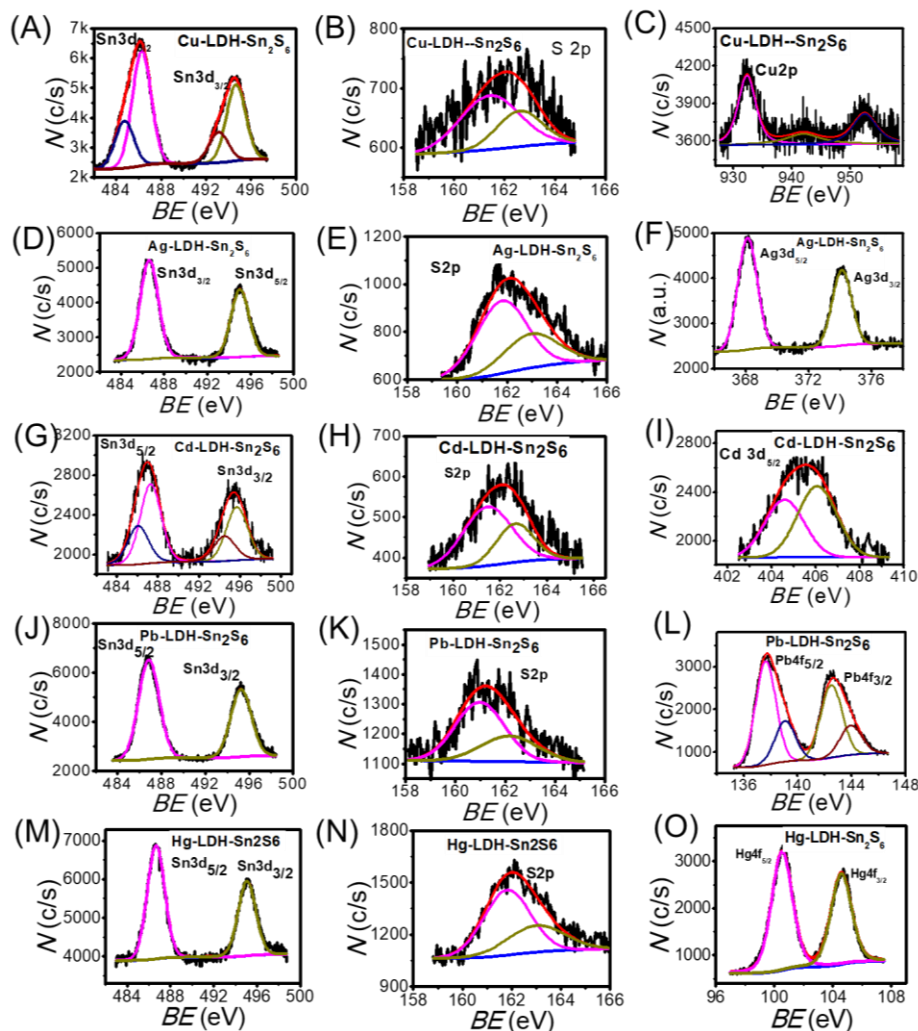


Figure 7. X-ray photoelectron spectra of LDH-[Sn₂S₆] after the adsorption of 100 ppm Cu²⁺ (A-C); Ag⁺ (D-F); Cd²⁺ (G-I); Pb²⁺ (J-L); and Hg²⁺ (M-O).

be assigned to Ag 3d^{5/2} and 3d^{3/2} respectively.^[79] The bands centered at 404.6 and 406.1 eV correspond to Cd 3d^{5/2}, and 3d^{3/2} obtained from the Cd²⁺ adsorbed sample.^[35, 79] For the Pb²⁺ adsorbed sample, deconvolution of the peaks shows bands centered at 137.67/139.10 and 142.50/143.95 eV, respectively. These peaks originate from the 4f^{7/2} and 4f^{5/2} binding energies of Pb²⁺.^[55] The energies of 137.67 and 142.50 eV (4f^{7/2} and 4f^{5/2}) correspond to the Pb²⁺ of PbS;^[55] while energies of 139.10 and 143.95 eV may originate from the 4f^{7/2} and 4f^{5/2} of Pb²⁺ with a

different chemical environment, probably in the vicinity of the oxides.^[80] The Hg²⁺-adsorbed sample reveals binding energies at 100.51 and 104.60 eV, which can be assigned as Hg 4f^{7/2} and 4f^{5/2}, respectively.^[79] All the post-adsorption samples revealed Sn 3d bands in the range of 483-495 eV.^[79] Deconvolution of the Sn 3d bands of Cu and Cd adsorbed samples yielded two sets of energy bands at 484.76/493.21 and 486.29/494.67 eV for Cu and 486.12/494.46 and 487.26/495.71 eV for Cd.^[55] For the Ag⁺, Pb²⁺, and Hg²⁺ adsorbed samples, only one set of bands of Sn 3d (3d^{5/2}, 3d^{3/2}) was observed. These bands are centered at 486.61/495.06, 486.88/495.2 and 486.65/495.07 eV for Ag⁺, Pb²⁺, and Hg²⁺, respectively.^[55, 79] The deviation of the binding energy of Sn 3d can be attributed to the diverse chemical environment of Sn⁴⁺ cations. Moreover, the deconvoluted spectra of S 2p of the post adsorptions samples exhibit the binding energies of 161.45 and 162.65 eV for Cu²⁺, 161.86 and 163.08 eV for Ag⁺, 161.52 and 162.70 eV for Cd²⁺, 161.01 and 162.23 eV for Pb²⁺, and 161.82 and 163.07 for Hg²⁺ (Figure 7).^[54, 55, 79] These values are shifted from the S 2p peaks of the pristine LDH-[Sn₂S₆] with the binding energies in the range of 158.16- 161.54 eV. These suggest that there is a notable change in the electronic states possibly attributed to the partial oxidation of S²⁻ and/ formation of metal-sulfides.^[80]

3.6 Analysis of the adsorption mechanisms of Mⁿ⁺ by LDH-[Sn₂S₆]

XRD patterns of the pristine and the adsorbed samples provide intrinsic information about the structural features of the adsorbents. The adsorption mechanisms were investigated with respect to extremely low ($\sim 1.0 \times 10^2$ ppb), medium ($\sim 1.0 \times 10^4$ ppb) and extremely high ($\sim 1.0 \times 10^6$ ppb) concentrations as shown in the scheme 1. At an extremely low concentration of Mⁿ⁺, LDH-[Sn₂S₆] retains its layered structure with a little expansion of the basal spacing. This indicates that the interlayered Sn₂S₆⁴⁻ anions trap the inferior Mⁿ⁺ cations forming anionic complexes which remain inside the LDH gallery. A similar phenomenon has been observed in LDH-MoS₄.^[45] With

the increase of the concentrations of M^{n+} (≥ 10 ppm), the $[Sn_2S_6]^{4-}$ would combine with the M^{n+} with a probable formation of electroneutral amorphous $\{M^{n+}[Sn_2S_6]^{4-}\}$ which moves out of the LDH gallery. Concomitantly, NO_3^- anions of the nitrate salt of the cations enter into the interlayers and thus the LDH- NO_3 regenerates. At concentrations ≥ 10 ppm, the adsorption mechanism probably varies with the type of M^{n+} . For example, 100 ppm adsorbed samples, XRD of Cu^{2+} and Ag^+ adsorbed samples show a single phase LDH- NO_3 , while for the Cd^{2+} , Pb^{2+} and Hg^{2+} adsorbed samples LDH- NO_3 coexists with the respective sulfides and sulfates (Figure S4). At extremely high concentrations (≥ 1000 ppm), the introduction of a large amount of metal ions destroys the layered structure of LDH. The M^{n+} cations bind with the S^{2-} decomposed from $[Sn_2S_6]^{4-}$ generating metal sulfides or sulfates, where the latter is formed by the oxidation of sulfides.

4. Application potential studied using tap and river water: To assess the effects of the high concentrations of the cations and anions as well as the feasibility of LDH- $[Sn_2S_6]$ to use for wastewater treatment, we studied the heavy metal uptake kinetics, selectivity, and efficiencies for tap and Mississippi river water (Table 4, Figure 8).

To perform this experiment, we spiked the tap water with a mixture of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} (Table 4) each at a concentration of 1 ppm, (1000 ppb; 8000 ppb in total). This experiment revealed LDH- $[Sn_2S_6]$ as an extremely efficient adsorbent for the concurrent removal of Cu^{2+} , Ag^+ , Pb^{2+} , Cd^{2+} , and Hg^{2+} . More precisely, in tap water, LDH- $[Sn_2S_6]$ can remove over 99.5% of Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} in seconds. Such an extremely rapid removal of cytotoxic Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} led to final concentrations of each cation of ≤ 5 ppb in less than 1 min (Figure 8A, Table 4) satisfying the WHO defined limit for safe drinking water. In 5 min, the removal capacity was increased to 99.8% for Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} resulting in final concentration of each cations as low as ≤ 2 ppb with K_d values remaining in the range of $\sim 10^5$ to 10^7 mL/g. Notably,

in comparison to Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} , the Cu^{2+} is less selective and it takes about 15 min to reduce its concentration down to 2 ppb. Hence, the selectivity order that we determined in tap water is Zn^{2+} , Co^{2+} , $\text{Ni}^{2+} \ll \text{Cu}^{2+} < \text{Hg}^{2+}$, $\text{Cd}^{2+} < \text{Pb}^{2+}$, Ag^+ which suggests that this material is extremely selective for the toxic Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} in tap water at ambient conditions and sorbes them within minutes.

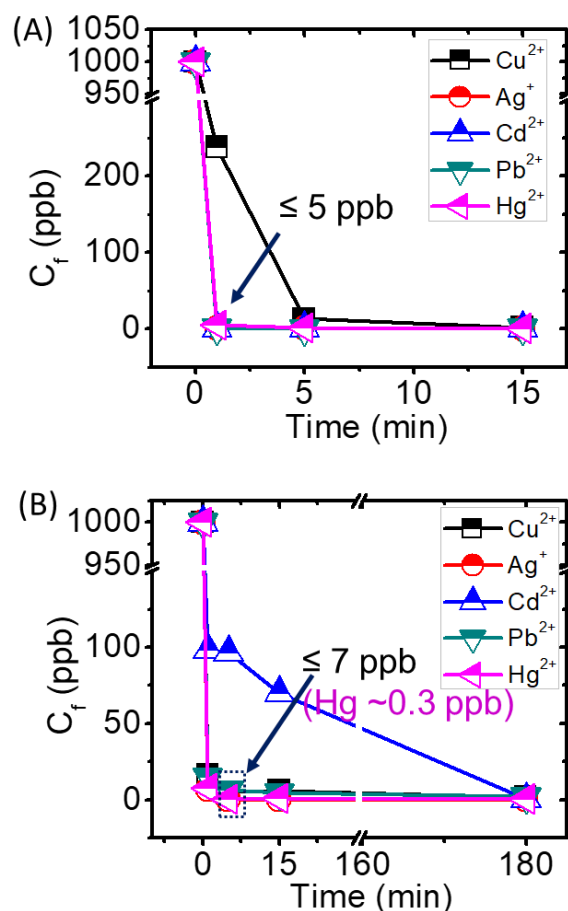


Figure 8. Concurrent adsorption kinetics curves of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} obtained in tap water (A) and Mississippi river water (B) showing the highly efficient and rapid removal of the toxic cations from ppm to ppb levels.

Moreover, we studied the Mississippi river water (collected from Vidalia, Louisiana) and found that despite the presence of major background ions of Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , CO_3^{2-} , SO_4^{2-} , NO_3^- and others, as well as a variety of organic species, LDH-[Sn_2S_6] shows an unprecedented sequestration of the Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} . In mixed-ion states of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} at concentrations of 1000 ppb for each (8000 ppb in total), LDH-[Sn_2S_6] stands out as extraordinary adsorbent for the simultaneous capture of Cu^{2+} , Ag^+ , Pb^{2+} , and Hg^{2+} from ppm to ppb level just in 5 min satisfying the safe drinking water limit defined by US EPA and WHO (Table 4, Figure 9B). In contrast, the adsorption kinetics of Cd^{2+} is relatively slow and after 3 h of interactions at mixed-states the residual concentrations of cadmium ion reach below one ppb. Our study shows that the selectivity order for the heavy metal cations of Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Hg^{2+} , Cd^{2+} , Pb^{2+} , Ag^+ for the tap water spiked solutions is Zn^{2+} , Co^{2+} , $\text{Ni}^{2+} \ll \text{Cu}^{2+} < \text{Hg}^{2+}$, $\text{Cd}^{2+} < \text{Pb}^{2+}$, Ag^+ while for the Mississippi river water it is Zn^{2+} , Co^{2+} , $\text{Ni}^{2+} \ll \text{Cd}^{2+} < \text{Cu}^{2+}$, $\text{Hg}^{2+} < \text{Pb}^{2+}$, Ag^+ . In both experiments, LDH-[Sn_2S_6] efficiently and concurrently sequestered Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} from the waters. However, the sorption kinetics were relatively slow for the river water suggesting that the presence of highly concentrated numerous cations, anions, and organic species can affect the adsorption of heavy metals ions. Overall, LDH-[Sn_2S_6] is an unprecedented adsorbent that exhibits rapid, efficient, and the concurrent removal of Ag^+ , Cu^{2+} , Pb^{2+} , and Hg^{2+} in the highly competitive ionic states of contaminated water of natural sources. Thus, this material can be used for the removal of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} at trace level during the water purification process.

Table 4. Adsorption results of LDH-[Sn_2S_6] toward mixed eight ions of 1 ppm for each (8 ppm total) in potable water and Mississippi river water, C_i = initial (pre-adsorption) concentration, C_f = final (post adsorption) concentration.

Mixed-ions	Time (min)	C _i (ppm)	C _f (ppm)	Removal (%)	K _d (mL/g)	C _f (ppm)	Removal (%)	K _d (mL/g)
			Tap water			Mississippi river water		
Co ²⁺	<1	1.0	0.8080	19.13	2.4×10 ²	0.9979	0.21	2.10
	5	1.0	0.6880	31.17	4.5×10 ²	0.9501	4.99	5.3×10 ¹
Ni ²⁺	<1	1.0	0.9990	0.06	6.0×10 ⁻¹	0.9573	4.27	4.5×10 ¹
	5	1.0	0.9150	8.51	9.3×10 ¹	0.8961	10.39	1.2×10 ²
Zn ²⁺	<1	1.0	0.9990	0.002	2.0×10 ⁻²	0.9913	0.87	8.8
	5	1.0	0.8650	13.48	1.5×10 ²	0.9902	0.98	9.9
Cu ²⁺	<1	1.0	0.2380	76.21	3.2×10 ³	0.0163	98.37	6.0×10 ⁴
	5	1.0	0.0130	98.74	7.8×10 ⁴	0.0050	99.50	2.0×10 ⁵
	15	1.0	0.0020	99.77	4.4×10 ⁵	0.0062	99.38	1.6×10 ⁵
Ag ⁺	<1	1.0	0.0001	99.99	1.0×10 ⁷	0.0070	99.30	1.4×10 ⁵
	5	1.0	0.0001	99.99	1.0×10 ⁷	0.0003	99.97	3.3×10 ⁶
	15	1.0	0.0001	99.99	1.0×10 ⁷	0.0001	99.99	1.0×10 ⁷
Cd ²⁺	<1	1.0	0.0040	99.62	2.6×10 ⁵	0.0985	90.15	9.2×10 ³
	5	1.0	0.0020	99.80	5.0×10 ⁵	0.0967	90.33	9.3×10 ³
	15	1.0	0.0001	99.99	1.0×10 ⁷	0.0700	93.00	1.3×10 ⁴
	180	-	-	-	-	0.0003	99.97	3.3×10 ⁶
Pb ²⁺	<1	1.0	0.0001	99.99	1.0×10 ⁷	0.0147	98.53	6.7×10 ⁴
	5	1.0	0.0001	99.99	1.0×10 ⁷	0.0066	99.34	1.5×10 ⁵
	15	1.0	0.0001	99.99	1.0×10 ⁷	0.0045	99.55	2.2×10 ⁵
	180	-	-	-	-	0.0002	99.98	5.0×10 ⁶
Hg ²⁺	<1	1.0	0.0049	99.51	2.0×10 ⁵	0.0078	99.22	1.3×10 ⁵
	5	1.0	0.0012	99.87	7.9×10 ⁵	0.0003	99.97	3.3×10 ⁶
	15	1.0	0.0008	99.92	1.2×10 ⁷	0.0005	99.95	2.0×10 ⁶

(LDH-[Sn₂S₆] ~ 0.01 g, volume of tap water 10 mL, v/m = 1000 mL/g and pH ~7)

To evaluate regeneration and reusability, LDH-Sn₂S₆ was investigated for the adsorption of the mixture of the solutions of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ in five consecutive cycles (Figure 9, Table S10). These experiments were conducted using the total initial concentrations of 50 ppm of the mixed cations of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ with 10 ppm of each element for each

cycle. Regeneration experiments were conducted using the 0.2 M EDTA as a complexing agent for heavy metals solutions after each cycle as described previously for Fe-MoS₄.^[68] The recycling experiments show that LDH-Sn₂S₆ can efficiently remove Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ for a number of consecutive cycles. Notably, from the first through 5th cycles, LDH-Sn₂S₆ removed over 99.9% of Ag⁺ and Hg²⁺ with K_d values of $\sim 10^6$ mL/g. In contrast, during the 5th cycle, LDH-Sn₂S₆ removed about 97.8% of Cu²⁺, 96.7% of Cd²⁺, and 90.3% of Pb²⁺ ions. A similar efficiency was also obtained for Ag⁺ sorption by Fe-MoS₄.^[68] These consecutive reuse experiments show that LDH-Sn₂S₆ remains efficient for the removal of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ even after five consecutive cycles.

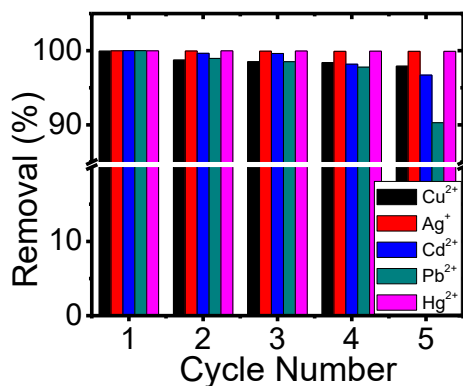


Figure 9: Recycling and separation of the heavy metals from a mixture of Cu²⁺, Ag⁺, Cd²⁺, Pb²⁺, and Hg²⁺ from aqueous solutions in five consecutive cycles.

To determine the leaching of Mg²⁺, Al³⁺ and Sn⁴⁺ from the solid sorbent to the solutions during the adsorption of heavy metal ions, we analyzed the solutions after the sorption experiments of mixed solutions of Cu²⁺, Ag⁺, Pb²⁺, Cd²⁺ and Hg²⁺ (Table S11). Leaching of Sn⁴⁺ resulted in a final solution concentration of 0.003 ppm which is equivalent to about 0.02% of total Sn in the sorbent. Greater solution concentrations were observed for Mg²⁺ (23.3 ppm) and Al³⁺ (9.7 ppm) corresponding to about 16 and 11%, respectively, of their total amounts in the solid matrix of LDH-Sn₂S₆. XRD of the solid sorbent after the adsorption shows the retention of LDH structure

which may demonstrate the topotactic exchange of the non-hazardous Mg^{2+} and Al^{3+} by heavy metal cations.

5. Conclusions

This study revealed the intercalation of the thiostannate anion, $[\text{Sn}_2\text{S}_6]^{4-}$, into the interlayer space of the solid-state matrix of LDHs using the chemistry of ion-exchange at ambient conditions. The soft polarizable Lewis basic characteristics of the sulfides (S^{2-}) of the thiostannate anions of this novel hybrid LDH- $[\text{Sn}_2\text{S}_6]$ exhibit tremendously high sorption and unprecedented selectivity for a wide number of Lewis acidic heavy metal cations. This material achieved over 99.9% concurrent uptake of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} from the mixed-ions state of DIW, tap water, and river water maintaining K_d values over 10^6 mL/g. Strikingly, even in the presence of a large variety of competitive ions in the river water, LDH- Sn_2S_6 simultaneously removed the cytotoxic Cu^{2+} , Ag^+ , Pb^{2+} , and Hg^{2+} down to the WHO defined limit for drinking water in only 5 min. Moreover, LDH- Sn_2S_6 can adsorb Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} with maximum sorption capacities of 378, 978, 332, 579, and 666 mg/g, respectively. Our study also revealed that LDH- $[\text{Sn}_2\text{S}_6]$ is remarkably effective in acidic and basic solutions, capturing of over 99% of Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} with K_d values of $> 10^5$ mL/g. The adsorption phenomena for Cu^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , and Hg^{2+} can be demonstrated by the pseudo-second-order models which indicate a chemisorption process *via* metal sulfide bonds is involved the adsorption of M^{n+} cations. The metal ion adsorption mechanism mainly includes the formation of interlayered $[\text{M}^{n+}\text{Sn}_2\text{S}_6^{4-}]$ complex and neutral metal-sulfides and depends on the M^{n+} : LDH- $\text{Sn}_2\text{S}_6^{4-}$ ratio. LDH- Sn_2S_6 is recyclable and can efficiently remove toxic heavy metal cations to ppb levels over at least five consecutive cycles. Overall, our results suggest that LDH- $[\text{Sn}_2\text{S}_6]$ is an unprecedented adsorbent that exhibits ultra-high heavy metal removal efficiencies, uptake kinetics, sorption capacity, robust selectivity,

and stability for a wide range of pHs. These fascinating findings place this cost-effective LDH–[Sn₂S₆] at the top of any adsorbents known to date, and thus could be used for the decontamination of heavy metal polluted wastewater.

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Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A. and Supplementary data: Supplementary data of this article can be found online at xxx

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Notes: The authors declare no financial interest

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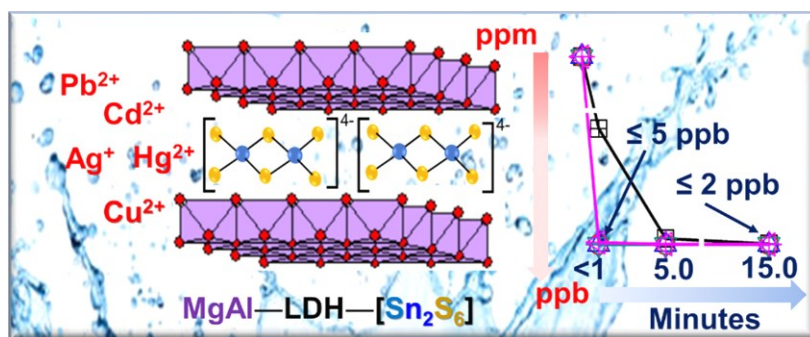
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TOC Graphic: LDH-[Sn₂S₆] is a unique adsorbent that combines an ultrahigh removal, superior selectivity, extremely rapid adsorption kinetics, a wide range of pH stability, and enormous adsorption capacity. The combinations of such extraordinary adsorption features place LDH-Sn₂S₆ at the top of all materials known to date. Thus, this material could be used for the decontaminations of wastewater.



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