



Efficient, stable and selective adsorption of heavy metals by thio-functionalized layered double hydroxide in diverse types of water

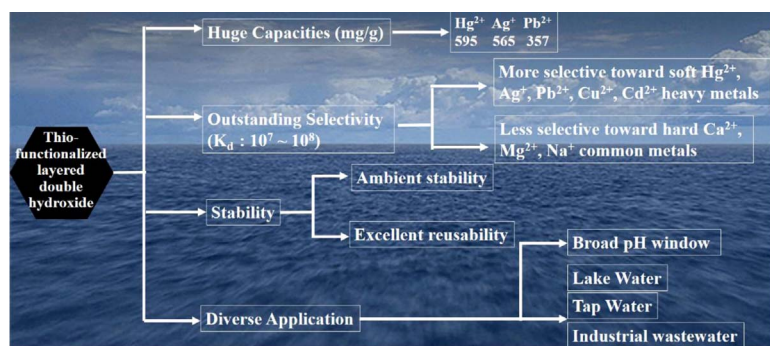


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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Adsorption
Thiol
Layered double hydroxide
Heavy metal ions
Selectivity

ABSTRACT

The designing of efficient, selective and stable adsorbents for heavy metals removal remained a challenging task, as most adsorbents did not exhibit consistent performance in diverse types of water. Unlike traditional adsorbents based on surface oxygen groups, thio-functionalized layered double hydroxide (LDH) as Mn-MoS₄ was designed by inserting MoS₄²⁻ anions into lamellar layers in LDH, and was applied as a highly stable, efficient and selective adsorbent for heavy metals removal. The record high distribution coefficient ($K_d \sim 10^7\text{--}10^8$ mL/g), fast kinetics and enormous saturated uptake capacities (594, 564 & 357 mg/g) for Hg²⁺, Ag⁺ and Pb²⁺ placed Mn-MoS₄ as the most efficient adsorbent for the removal of such metals so far. Further, Mn-MoS₄ can completely tolerate the impact of huge concentration of background electrolytes (Ca²⁺, Mg²⁺, Na⁺, Cl⁻, NO₃⁻ & SO₄²⁻), and effectively control the concentrations of Hg²⁺, Ag⁺ and Pb²⁺ ions from tap water, lake water or industrial wastewater far below the limitation in drinking water. Similarly, Mn-MoS₄ is a potential filter due to its consistent performance over a broad pH range (from 2.0 to 11.0), changing ionic strength (up to 100 mM) or in the presence of organic matters. These remarkable features originate from the dominant chemical adsorption mechanism through inner-sphere coordination between thio groups as soft Lewis acid and Hg²⁺, Ag⁺ and Pb²⁺ as soft Lewis bases. More interestingly, LDH layers offer protective space for intercalated MoS₄²⁻ anions against oxidation, and facilitate Mn-MoS₄ with the advantage of easy storage and application over other adsorbents.

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<http://dx.doi.org/10.1016/j.cej.2017.09.080>

Received 28 July 2017; Received in revised form 9 September 2017; Accepted 11 September 2017

Available online 15 September 2017

1385-8947/ © 2017 Published by Elsevier B.V.

1. Introduction

The removal of heavy metal ions from aqueous medium has attracted considerable research interests because of its detrimental effects on both human beings as well as aquatic lives [1]. Amongst various technologies developed over the years, adsorption is considered as the most attractive one due to facile engineering, low cost and relatively high efficiency in diverse levels of contamination [2–4]. Classic adsorbents include metals oxides [1], activated carbon [5], sewage sludge biochar [6], amino modified biochar [7], zeolites [8], polymers [9], biomaterials [10], and clays [11]. However, early reports of these adsorbents generally offered slow kinetics and low capacities. Additionally, the performances of these adsorbents are not stable when being applied in diverse types of water because the competitive adsorption of background electrolytes (Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}) seriously disturbs the selective removal of heavy metal. On the other hand, change of water quality in pH, ionic strength, organic content, etc may also negatively influence the stability and/or efficiency. These emerged drawbacks are attributed to the chemi-physical mechanism of traditional adsorbents: 1) the chemical interaction between adsorbents and transitional metal ions was commonly based on the coordination effect through surface oxygen-containing groups. According to HSAB (hard and soft acids and bases) theory, oxygen-containing groups were considered as hard Lewis acid, and selectively bound hard Lewis base (Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}) rather than soft Lewis base (late transition metals such as Ag^{+} , Pb^{2+} and Hg^{2+}); 2) the physical adsorption based on electrostatic attraction was naturally influenced by change of water quality in pH and ionic strength.

Comparing with surface oxygen-containing unit, thio groups, $(-\text{S}-)^{2-}$ are softer acid in HASB theory, which favors the selective adsorption for late transition heavy metals because of the soft-soft coordination interaction. Metals sulphides such as $\text{K}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$ [12], $\text{K}_{2x}\text{Mg}_x\text{Sn}_{3-x}\text{S}_6$ [13], $\text{K}_{2x}\text{Sn}_{4-x}\text{S}_{8-x}$ [14], K–Pt– S_x chalcogen have been developed based on this concept [15]. However, thio groups usually suffer from the stability issue, that is, thio-functionalized adsorbents are highly sensitive to atmospheric oxygen. Thus, thio groups may be oxidized into sulfur oxides or dioxides and lose the selectivity [16–20], which consequently limits their environmental applications in real water treatment. To solve the issue of stability, one way is to physically exclude air during the storage and adsorption processes [21–23], which is obviously expensive and unpractical for field applications. The other way is to incorporate thio groups into chemically protective materials to enhance the stability under mild conditions.

Recently, layered double hydroxide (LDH) has attracted considerable attentions due to its extraordinary ion-exchange ability, large surface area and simple preparation method, and has been applied in multiple chemical and environmental engineering processes including adsorption for heavy metal removal [24–30]. More importantly LDH materials can be intercalated with different compounds such as crown ether [29], mercapto carboxylic acid [31], lignin [32], EDTA [33] and sulfur [21,34]. In this regard, binding thio groups chemically into protective lamellar LDH structure can provide protection against solubility as well as for direct oxygen exposure. More recently, Kanatzidis group has applied a novel concept by introducing MoS_4^{2-} anions in the layered structure of bi-metallic MgAl [34–36]. The resultant MgAl-MoS₄ was not only the most efficient material developed so far to capture heavy metals but also demonstrated application in the removal of toxic anionic species from aqueous medium.

In this paper, we developed an efficient, stable and selective process of adsorption based on a novel adsorbent of Mn-MoS₄ by introducing the redox metals such as Mn into the traditional MgAl-LDH structure, and intercalated with MoS_4^{2-} anions. This approach allows firstly to modulate the ion exchange features of simple bimetallic MgAl-LDH due to variable oxidation states (i.e. Mn^{2+} , Mn^{3+} or Mn^{4+}). Secondly, tri-metallic LDH with Mn is expected to withstand more diverse conditions of different types of water (acidic or basic pH, competitive cations,

anions & organic matrix). Thirdly, the fabrication of manganese ($\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$) in the LDH structure would change the charge density of metallic layers that may affect the stability of intercalated MoS_4^{2-} anions. As expected, Mn-MoS₄ indeed exhibited record high distribution coefficient, fast kinetics, enormous saturated uptake capacities for Hg^{2+} , Ag^{+} and Pb^{2+} , excellent re-usability, pH window (from 2.0 to 11.0) and these attractive features of Mn-MoS₄ led to its remarkable performance toward diverse types of water including tap water, lake water and different industrial wastewater.

2. Material and experimental section

2.1. Chemicals

Analytical grade nitrate salts of Mg^{2+} , Mn^{2+} and Al^{3+} were purchased from Sinopharm Chemical Reagent Co. Ltd (China). Analytical grade nitrate salts of Co^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Ag^{+} , Cu^{2+} and Cd^{2+} were purchased from Adamas Reagent Co. Ltd. Ammonium tetramolibdate ($(\text{NH}_4)_2\text{MoS}_4$) (99.95%) and NaNO_3 were purchased from Energy chemical Co. Ltd (China).

2.2. Preparation of Mn-MoS₄

Generally, magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in 50 mL de-ionized water to yield a total metal ions concentration 9.4 mM (5.4: 1.0: 3.0). Then HMT (5.9 mM in 50 mL) was introduced before transferring to autoclave for hydrothermal treatment at 140 °C for 24 h. After centrifugation and washing, the light white colored Mn-CO₃ solid was vacuum dried at 60 °C for 24 h. From ICP and CHN analysis, the derived chemical formula for Mn-CO₃ LDH was $\text{Mn}_{0.08}\text{Mg}_{0.64}\text{Al}_{0.28}(\text{OH})_2(\text{CO}_3)_{0.22} \cdot 0.14\text{H}_2\text{O}$ (Table S1).

The de-carbonization of Mn-CO₃ to Mn-NO₃ was conducted through ion exchange method. First, 0.8 g of Mn-CO₃ was dispersed in aqueous solution (800 mL) containing 1.5 M NaNO_3 and 4 mM HNO_3 . The suspended solution was kept on gentle shaking for 24 h after purging with Ar gas at ambient condition. The resulting Mn-NO₃ LDH was washed with deionized water and finally dried in vacuum at 60 °C. The composition analysis as conducted on ICP and CHN suggested the chemical formula of $\text{Mn}_{0.08}\text{Mg}_{0.64}\text{Al}_{0.28}(\text{OH})_2(\text{NO}_3)_{0.34}(\text{CO}_3)_{0.05} \cdot 0.17\text{H}_2\text{O}$ for Mn-NO₃ LDH (Table S1).

For Mn-MoS₄, the NO_3^- anions of Mn-NO₃ were exchanged by MoS_4^{2-} anions coming from $(\text{NH}_4)_2\text{MoS}_4$. Typically, 0.2 g of $(\text{NH}_4)_2\text{MoS}_4$ and 0.2 g of Mn-NO₃ were first dispersed in 10 mL degassed de-ionized water. Then the obtained suspension was allowed to shak at room temperature for 24 h. The resulting Mn-MoS₄ solids were centrifuged, washed with de-ionized water and finally dried in vacuum at 60 °C for 24 h. The chemical formula of $\text{Mn}_{0.08}\text{Mg}_{0.64}\text{Al}_{0.28}(\text{OH})_2(\text{NO}_3)_{0.02}(\text{CO}_3)_{0.06}(\text{MoS}_4)_{0.15} \cdot 0.24\text{H}_2\text{O}$ was derived for Mn-MoS₄ after composition analysis on ICP and CHN (Table S1).

2.3. Characterization techniques

The XRD pattern of prepared materials was recorded on PAN analytical, X'Pert PRO diffractometer. Fourier Transform Infrared Spectra (FTIR) was collected for samples on Bruker Equinox 55 spectrometer using the KBr pellet method. Raman spectra of the samples were analyzed on microscopic confocal Raman spectrometer. The Scanning Electron Microscopy (SEM) was carried out on SEM Virion 200. BET surface area was analyzed on Quanta chrome NOVA 3200e. Similarly X-ray photoelectron spectroscopy (XPS) was conducted on V.G scientific ESCALAB mark II system. The metals ions composition for Mn-CO₃, Mn-NO₃ and Mn-MoS₄ were analyzed on ICP (Perkin Elmer optima 8300) while elemental analysis was conducted on Elementar Vario EL elemental analyzer for C, H, N and S analysis.

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