

Article

Adsorption and Reduction of Aqueous Cr by FeS-Modified Fe-Al Layered Double Hydroxide

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Abstract: To remedy the widespread chromium (Cr) pollution in the environment, this study mainly used the ultrasonic-assisted co-precipitation and precipitation methods to prepare FeS-modified Fe-Al-layered double hydroxide (FeS/LDH) composite material. The experimental results showed that FeS/LDH has higher removal efficiency of Cr in aqueous solution and stronger anti-interference ability than unmodified LDH. Under the same reaction conditions, the removal efficiency of total Cr(Cr(T)) using LDH was 34.85%, and the removal efficiency of Cr(VI) was 46.76%. For FeS/LDH, the removal efficiency of Cr(T) and Cr(VI) reached 99.57% and 100%, respectively. The restoration of Cr(T) and Cr(VI) by FeS/LDH satisfied the Langmuir adsorption isotherm. The maximum adsorption capacity of Cr(T) and Cr(VI) achieved 102.9 mg/g and 147.7 mg/g. The efficient removal of Cr by FeS/LDH was mainly based on the triple synergistic effect of anion exchange between Cr(VI) and interlayer anions, redox of Cr(VI) with Fe^{2+} and S^{2-} , and co-precipitation of Fe^{3+} and Cr^{3+} .

Keywords: chromium; FeS/LDH; double reduction; anti-interference; co-precipitation



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1. Introduction

Heavy metal pollution is a major pollution problem that threatens people's health [1,2]. Since heavy metal ions cannot be biodegraded, they can accumulate in an organism along with transfer to the ecosystem and have an indelible impact on human health [3,4]. Chromium (Cr) is a common heavy metal pollutant in soil and water that has been identified as a human carcinogen by the International Agency for Research on Cancer [5]. Cr(III) exists in the form of Cr_2O_3 , which can form precipitates or complexes into other substances and stably exists in water or soil [6]. Cr(VI) mainly exists in the environment in the form of CrO_4^{2-} and HCrO_4^- [7]. The toxicity of Cr(VI) is 100 times greater than Cr(III) [8,9]. Cr(VI) combines with enzymes in the body and destroys the catalytic effect of enzymes [10]. Cr(VI) affects the normal oxidation–reduction process of the human body and has obvious carcinogenic effects [10]. Cr(III) is an essential trace element for the human body, and its complex is called the human body's “glucose tolerance factor”, which helps to improve the level of glucose tolerance [11].

In recent years, numerous treatment techniques have been developed to deal with Cr pollution from the aquatic ecosystems, such as adsorption [12], ion exchange treatment [13], chemical precipitation [14–16], bio-removal [17], and membrane filtration [18]. Among these, chemical fixation technology has attracted more attention due to its convenient operation, high efficiency, low secondary pollution, and relatively low cost [14–16]. So far, layered double hydroxide (LDH) has been widely studied for removing Cr. LDHs are a group of anionic clay materials with the general formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ [19,20]. M^{2+} (Mg^{2+} , Mn^{2+} , Fe^{2+} , Zn^{2+} , Cu^{2+} , etc.) and M^{3+} (Al^{3+} , Fe^{3+} , Co^{3+} , etc.) represent divalent cations and trivalent cations, respectively. A^{n-} (CO_3^{2-} , Cl^- , NO_3^-) represents the interlayer anion [19,21]. To synthesize hydrotalcite materials, the molar ratio of M^{3+} and M^{2+} + M^{3+} is 0.2–0.33 [22]. Therefore, LDH can be prepared only when the molar ratio of M^{2+} and M^{3+} = 2 or 3. In an anionic environment, LDH exhibits excellent anion exchange properties

due to the weak electrostatic interaction between the cations and interlayer anions [23,24]. Therefore, LDH is an attractive candidate to be applied in the removal of inorganic anionic pollutants including Cr [25,26].

In recent years, many researchers have used LDH as an absorbent to capture anionic pollutants in water: Gao et al. found that the fixation ability of sand Mg-Al-LDH for Cr(VI) was 29.9 mg/g [27]. Xu et al. found that the repairability of single-layer Ca LDH and Mg LDH for Cr(VI) was 56.2 mg/g and 47.9 mg/g, respectively [28]. Fe₃O₄-ZnAl LDH reported by Yang et al. could fix Cr(VI) at 47.3 mg/g [29]. Mg-Al-MoS₄ LDH studied by Ma et al. could remove Cr(VI) at 130 mg/g [30]. Among them, some studies utilized ion-exchange properties of LDH to fix heavy metal anions between layers. Some studies used LDH as reactive media to enhance the reduction of Cr(VI) to the more stable and less toxic Cr(III) [27–33].

In order to further improve removal efficiency, we urgently need to find a removal agent that is simple to prepare, low in cost, and capable of removing Cr. In this study, FeS-modified Fe-Al LDH composite (FeS/LDH) was selected as the Cr absorbent. Pristine Fe-Al LDH has ion exchangeability of hydrotalcite, as well as reduction properties of Fe²⁺. Meanwhile, the introduction of FeS on LDH layers can not only assist the better dispersion of FeS nanoparticles to avoid agglomeration, but also improve the reduction properties of the material. It was expected that the FeS-modified Fe-Al LDH shows improvement in ion exchange capacity and removal efficiency from the dual reduction capacity of Fe²⁺ and FeS [30,34].

2. Materials and Methods

2.1. Materials and Equipment

All chemical reagents used were of analytical grade or higher without further purification. Potassium dichromate (K₂Cr₂O₇) was supplied by Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. (Tianjin, China). Ferrous chloride (FeCl₂·4H₂O) was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Crystalline aluminum chloride (AlCl₃·6H₂O) and reduced iron powder (Fe) were purchased from Tianjin Komio Chemical Reagent Co, Ltd. (Tianjin, China). Nonahydrate sulfide Sodium (Na₂S·9H₂O) was obtained from Aladdin Reagent (Shanghai, China). Sodium hydroxide (NaOH) was purchased from Xilong Chemical (Guangdong, China). Chromium standard solution was supplied by the National Nonferrous Metals and Electronic Materials Analysis and Testing Center (Beijing, China).

The equipment used in this article mainly includes: TAS-990 atomic absorption courseware spectrophotometer from Beijing Jinko Company (Beijing, China); 772G visible light spectrophotometer of Shanghai Jinko Company (Shanghai, China); the model of Orion Instrument Company (Zhejiang, China) is a PHS-3C pH meter.

2.2. Preparation of Fe-Al LDH and FeS/LDH Composite Materials

Fe-Al LDH was synthesized according to an ultrasound-assisted co-precipitation method reported previously [35]. In brief, a suspension was prepared first by adding 4 M NaOH into 100 mL FeCl₂/AlCl₃ solution with a molar ratio of 2:1 until the pH reaches 10. Then, an appropriate amount of reduced iron was introduced to minimize the oxidation of Fe²⁺. Next, the mixture was sonicated at 65 °C for 30 min, filtered and washed with ultrapure water 3 times and dried. According to various Fe to Al ratios, the products were labeled as LDH2 (2:1) and LDH3 (3:1), respectively.

The precipitation method was used to synthesize FeS in situ on LDH [36]. First, a certain amount of the above prepared LDH was dissolved in 100 mL of water. Under magnetic stirring, 0.5 M FeCl₂ and 0.5 M Na₂S were added. The solution was stirred for 30 min and ultrasound for 2 h. Then, the mixture was filtered and washed with ultrapure water 3 times and dried. The resulting composite material was labeled as FeS/LDH. Both as-prepared LDH2 and LDH3 were modified by FeS using the same procedure, named as FeS/LDH2 and FeS/LDH3.

2.3. Characterizations

Fourier transform infrared spectra (FTIR, Thermo Nicolet IR200, Waltham, Massachusetts, USA) were recorded in the range of 4000–500 cm^{-1} to measure LDH, FeS/LDH and FeS materials after adsorption of Cr to study the interaction between LDH and FeS/LDH; the crystal structure which adopts X-rays diffraction (XRD, D8ADVANCE, Madison, USA) was used to study the XRD spectra obtained with JADE 6.0. X-ray photoelectron spectroscopy (XPS) measurement was performed to identify the functional groups on the surface of materials (XPS, Escalab 250 xi, Thermo Fisher Science, Waltham, MA, USA) with binding energy between 0 and 1200 eV to analyze the elemental composition of sample surfaces. The morphological characteristics of the samples were obtained using scanning electron microscopy (SEM) combined with an X-ray spectrometer (EDS) (SEM and EDS, FEI Company QUANTA Q400, Hillsboro, OR, USA). The point of zero charges of samples was determined for judging the charged condition of the material surface.

2.4. Batch Adsorption Experiment

The Cr solution used in the experiment was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. To prepare a removing agent with lower cost and better performance, the effect of FeS/LDH on Cr removal was studied from the aspects of pH, Cr concentration, and coexisting anions. During the experiment, FeS/LDH powder was added to the simulated Cr-polluted water, and the pH of the Cr solution was adjusted with 0.1 M HCl and 0.1 M NaOH. The mixture was placed on a magnetic stirrer for 24 h, followed by centrifuge. The supernatant was collected to determine the content of Cr(T) by flame atomic absorption spectrophotometry, as well as the content of Cr(VI) using diphenyl carbazide spectrophotometry. Cr removal efficiency was calculated based on the equation: $\eta = ((C_1 - C_2)/C_1) \times 100\%$ (where η is the removal efficiency of Cr(T) or Cr(VI), C_1 is the concentration of Cr(T) or Cr(VI) in the simulated polluted wastewater before removal (mg/L), C_2 is the concentration of Cr(T) or Cr(VI) in the solution after removal (mg/L)). All the experiments were repeated three times to confirm the results.

3. Results and Discussion

3.1. Characterizations

The Fourier Infrared Spectroscopy (FTIR) diagrams of LDH and FeS/LDH are shown in Figure 1a. Both of the two substances have peaks of Fe-O bond and Al-O bond at 560 cm^{-1} , 800 cm^{-1} , and 3380 cm^{-1} . There is one OH bond. These are the characteristic peaks of LDH; in addition, there is a peak of SO bond at 1060 cm^{-1} and a peak at 2950 cm^{-1} caused by SH-stretching vibration on FeS/LDH3 [31,35,37]. The XRD pattern (Figure 1b) also showed similar spectral characteristics, and the original peaks No. 003, 006, and 009 were added with the characteristic peak No. 101. These characteristics all indicate that FeS was successfully precipitated in the layer of LDH [36–38].

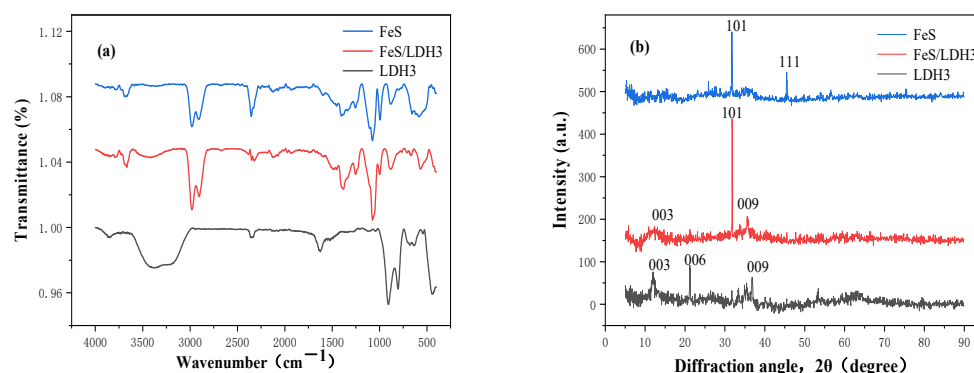


Figure 1. FTIR spectrum (a) and XRD patterns (b) of LDH3, FeS/LDH3, and FeS.

The LDH3 and FeS/LDH3 used in this study were characterized by SEM. LDH3 and FeS/LDH3 were selected for characterization because of their better performance in removal efficiency, which is discussed in Section 3.2.1 below. As shown in Figure 2a, the pristine LDH3 has a monolayer sheet structure with an average size of 230 nm [28]. After FeS modification, the flake-like structure of LDH3 (Figure 2b) is not clear. The surface of the material is relatively rough due to the formation of FeS nanoparticles. The morphology change can be attributed to sulfidation and agglomeration of FeS precipitates [36]. It can also be concluded from the X-ray energy spectrum (EDS) image of the material (Figure 2c) that according to the fluorescence phenomenon, Fe, Al and S are uniformly distributed in the material.

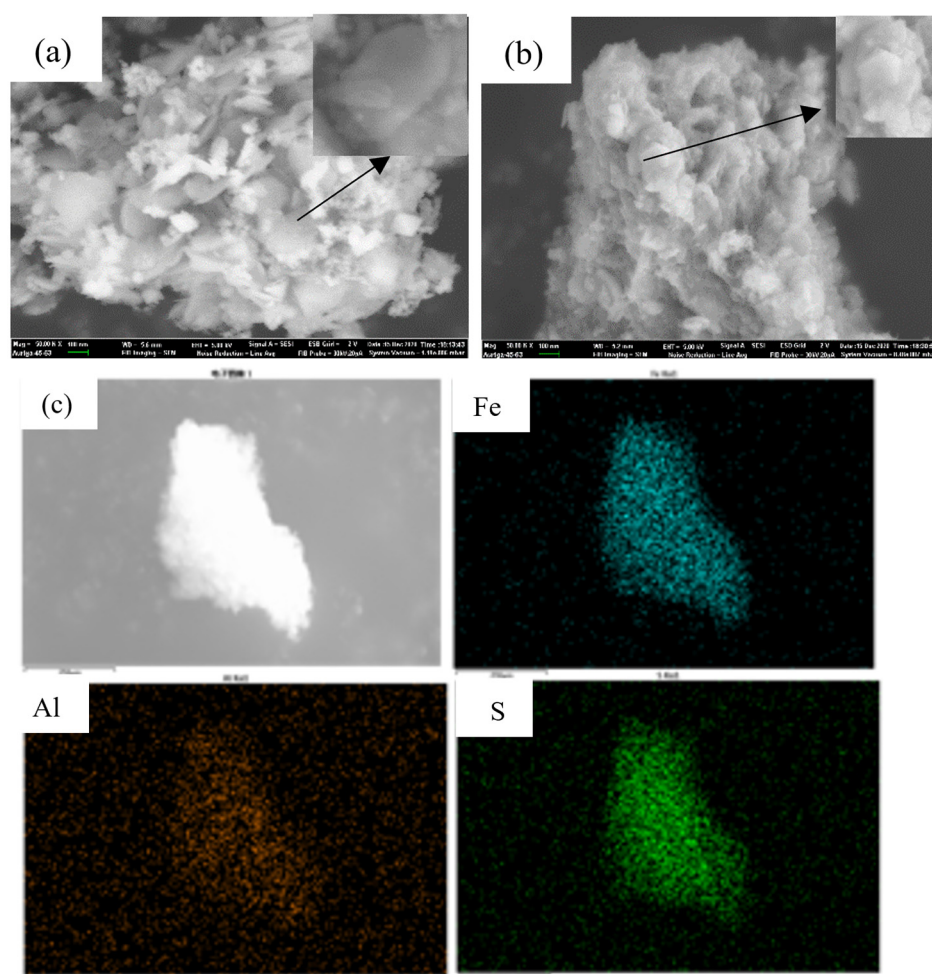


Figure 2. SEM images of (a) LDH3, (b) FeS/LDH3 and EDS images of (c) FeS/LDH3.

In Figure 3, XPS was applied to analyze the elements in FeS/LDH3. The results showed that the energy spectrum of Fe 2p had two peaks at 711.3 eV (FeS, 76.08%) and 724.6 eV (FeOOH, 23.91%) according to Figure 3b, indicating the successful synthesis of FeS in the composite [32,37]. The peak area of FeS is larger than FeOOH, suggesting a majority of FeS in the composite. There were three peaks in the energy spectrum of S 2p (Figure 3c), which were at 161.8 eV, 164.0 eV, and 167.7 eV. The peaks can be attributed to S^{2-} (69.33%), SO_3^{2-} (0.94%), and SO_4^{2-} (29.73%), respectively [39,40]. Comparing the peak areas, FeS was the main form of S in the material. In addition, the peaks of SO_4^{2-} and FeOOH appeared because air was not eliminated during the synthesis process, which led to the oxidation of S^{2-} and Fe^{2+} .

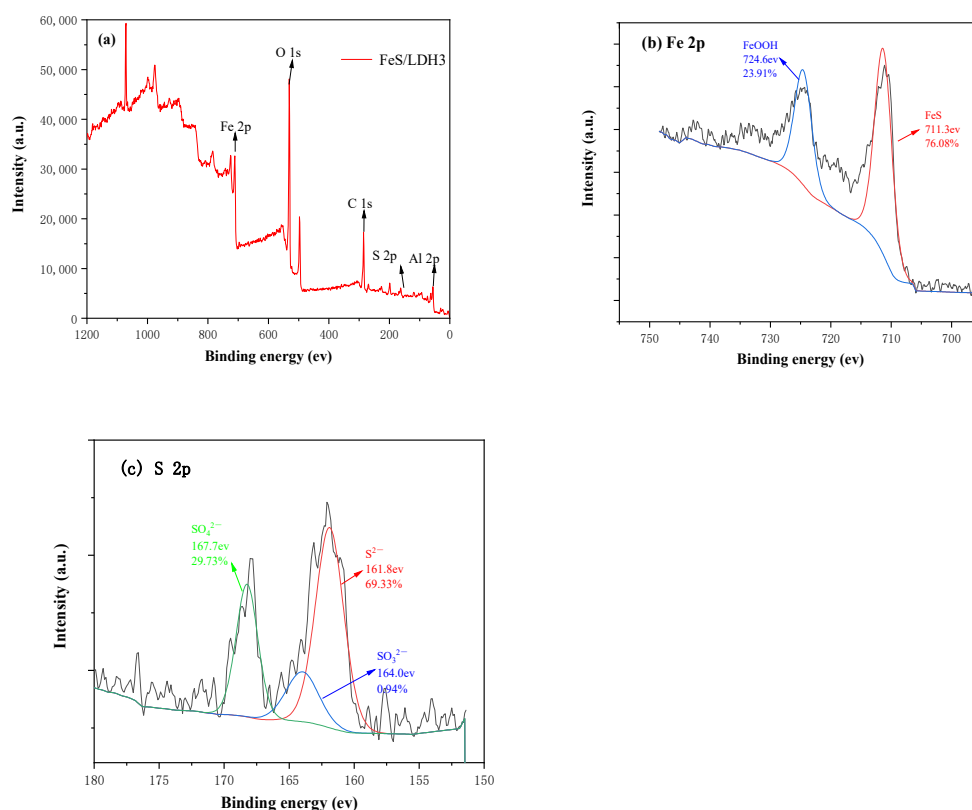


Figure 3. XPS full-spectrum (a), Fe 2p (b) and S 2p (c) spectra of FeS/LDH3.

Therefore, according to all the characterization results, FeS was successfully precipitated on the single-layer LDH. In this way, the layered structure of LDH can be used to deposit FeS smoothly, and the agglomeration of FeS can be effectively avoided.

3.2. Batch Adsorption Experiment

3.2.1. Ratio of Fe and Al in LDH

To evaluate the effect of Fe/Al molar ratio in LDHs on the performance of Cr removal, a series of experiments was carried out with an initial Cr concentration of 100.0 mg/L, a solid-to-solution ratio of 2.0 g/L, and an initial pH value of 9.0. Both pristine and modified LDHs with an Fe/Al molar ratio of 2 or 3 were applied in this study (Figure 4a,b). For all materials, the progress reached 90% within 2 h of the reaction, but to ensure that the reaction is fully completed, the subsequent measurement time is set to 24 h. Comparing the pure LDHs, LDH3 has higher removal efficiency of Cr(VI) (50.36%) and Cr(T) (65.23%) than LDH2 (Cr(T): 34.85%; Cr(VI): 46.76%). For modified composites, FeS/LDH3 synthesized by LDH3 shows Cr(VI) and Cr(T) removal efficiency of 99.58% and 100%, which are 99.15% and 92.28% higher than FeS/LDH2. The ratio of Fe^{2+} in LDH2 is lower than in LDH3. Fe^{2+} can reduce Cr(VI) to Cr(III), which tends to co-precipitate with Fe^{3+} to achieve effective capture of Cr(VI) [41,42]. Thus, FeS/LDH3 with a higher proportion of Fe^{2+} exhibited the fastest Cr removal. This is because the content of Fe^{2+} in LDH3 is greater than that of Fe^{2+} in LDH, LDH3 has a stronger reducing ability and a stronger removal efficiency of Cr(VI).

Therefore, compared with LDH, FeS/LDH is better. When analyzing the specific content of FeS/LDH, it is found that Fe: Al = 3 (FeS/LDH3) has a better effect. Among all materials, FeS/LDH3 is the most effective. To optimize the absorbent performance, the ratio of 3 for Fe and Al in the LDH was used in the following experiments.

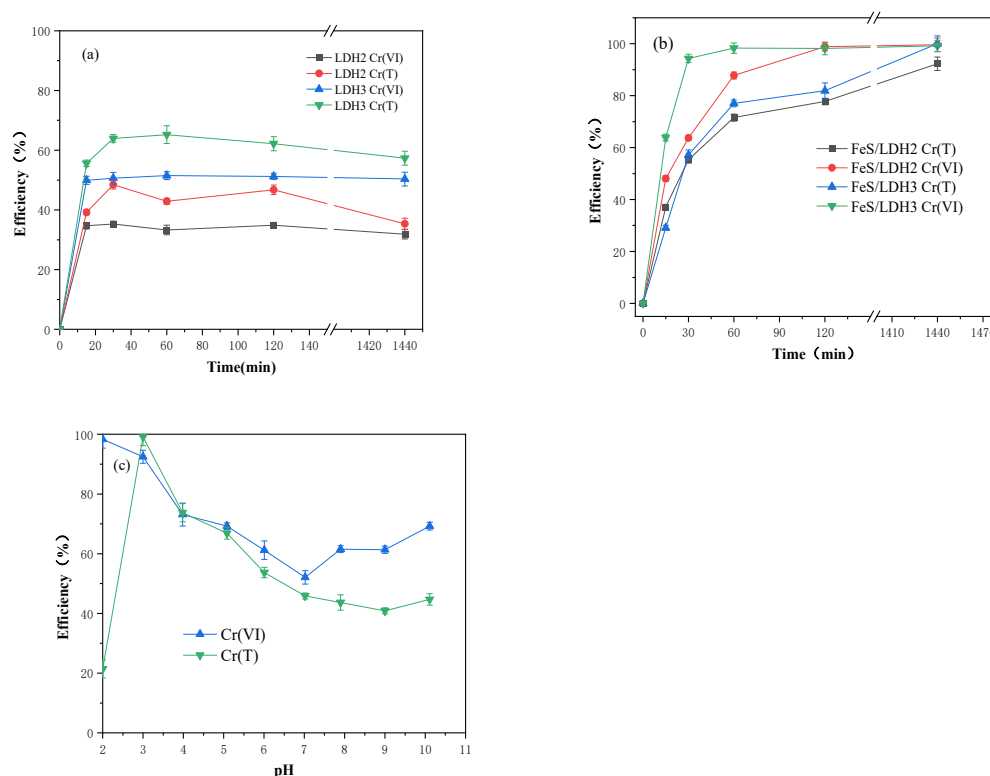


Figure 4. Effect of Fe: Al ratio (a,b) and pH (c) on removal efficiency of LDH3 and FeS/LDH3.

3.2.2. Influence of Initial pH

The effect of pH was explored by adjusting the solution pH from 2.0 to 10.0 using 0.1 M HCl and 0.1 M NaOH under an initial Cr concentration of 100.0 mg/L, a solid-to-solution ratio of 1.0 g/L, and a reaction time of 24 h. The pH range selection in this chapter is appropriately expanded based on the pH range of the polluted water. This ensures that the material can achieve better results within the maximum range. The results are presented in Figure 4c. At a pH value of 2.0, the removal efficiency of Cr(VI) reaches 98%. Meanwhile, the removal efficiency of Cr(T) is only 20%, indicating Cr(T) content in the solution is still high. The difference can be attributed to the increase in Cr^{3+} by the reduction of Cr(VI). At low pH, Cr^{3+} can neither precipitate nor co-precipitate with Fe^{3+} , resulting in a large amount of Cr^{3+} in the solution [11,43]. This is evident by the decreasing removal efficiency with increasing pH from 3 to 7 [44]. This is because the deprotonation effect of hydrotalcite gradually increases, resulting in a decrease in H^+ on the surface of hydrotalcite, thereby reducing anion exchange capacity and adsorption site saturation. At a pH ranging from 7 to 10, the removal efficiency of Cr(T) and Cr(VI) slightly increased. The adsorption of anions by LDHs materials is related to the valence of the anions. This is because as pH increases, Cr(VI) in the solution changes from HCrO_4^- to CrO_4^{2-} . CrO_4^{2-} is more negatively charged and can enter the ion exchange layer more easily [45,46]. Therefore, the Cr removal efficiency is improved.

3.2.3. The Modification with FeS

The Cr adsorption efficiencies for LDHs before and after FeS modification are studied in Cr polluted system with the initial Cr concentration of 200.0 mg/L, a solid-to-solution ratio of 1.0 g/L, and an initial pH value of 3.0. The Cr removal performance of pure FeS is also included, as shown in Figure 5a. It is clear that FeS/LDH has superior Cr removal performance (Cr(VI): 54.7%; Cr(T): 53.4%) over unmodified LDH (Cr(VI): 21.4%; Cr(T): 18.4%) and FeS (Cr(VI): 28.7%; Cr(T): 15.5%). Incorporating FeS on the surface of LDH can not only avoid the agglomeration of FeS through the large specific surface area of

LDH, but also take advantage of the reduction properties of FeS to enhance Cr(VI) removal performance of the FeS/LDH composite [40].

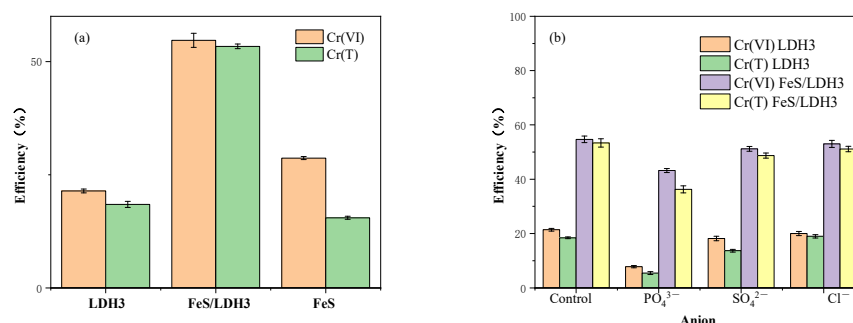


Figure 5. Effect of FeS (a) and coexisting anions (b) on the Cr removal efficiency of LDH3, FeS/LDH3 and FeS.

3.2.4. Coexisting Anions

In natural wastewater, there are other soluble ions such as Cl^- , SO_4^{2-} , and PO_4^{3-} , that could competitively affect the Cr removal by adsorbents. Therefore, we choose to carry out repair experiments in the presence of these ions. To explore the impact of various coexisting ions on Cr removal, 200 mg/L Cr solutions with each of Cl^- , SO_4^{2-} , and PO_4^{3-} at a certain concentration (200 mg/L) were prepared. The solid solution ratio was 1.0 g/L, and the initial pH was 3 [31]. The results are shown in Figure 5b. According to the plot, the performance of LDH was largely affected by the examined coexisting anions, especially PO_4^{3-} and SO_4^{2-} . For comparison, the removal efficiency of FeS/LDH was well maintained. This is because the Cr removal mechanism of LDH and FeS/LDH is based on the synergetic effect of interlayered ion exchange and reduction. In the presence of PO_4^{3-} , the Cr(T) and Cr(VI) removal efficiency of LDH was depressed by 70.44% and 63.16%, respectively, and the Cr(T) and Cr(VI) removal efficiency of FeS/LDH was depressed by 31.99% and 20.97%, respectively. The high-valent anions PO_4^{3-} and SO_4^{2-} are more favorable for interlayer anion exchange than low-valent anions such as Cl^- . Compared with the two ions of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, PO_4^{3-} and SO_4^{2-} had a higher valence and was less likely to be exchanged with Cr(VI), so Cr(VI) had fewer reaction sites and lower reaction efficiency. Thus, PO_4^{3-} and SO_4^{2-} competed with Cr(VI) more significantly in the adsorption process and the subsequent reduction [5]. After modification, the Cr(VI) reduction was promoted by FeS/LDH, where both Fe(II) and S(-II) species act as reducing agents. The buffer effect leads to a smaller decrease in Cr removal efficiency by coexisting anions.

3.2.5. Cr Concentration

The maximum unit Cr adsorption capacity of FeS/LDH was explored under an initial pH of 3.0, a solid-to-solution ratio of 1.0 g/L, and a reaction time of 24 h. The results are presented in Figure 6. As the Cr concentration increased, the unit adsorption capacity increased. The Langmuir adsorption equation was imitated for simulating the adsorption of Cr(VI) and Cr(T): $C/Q_e = 1/Q_m \times C + 1/(Q_m \times b)$, where C is the concentration of Cr(T) or Cr(VI), Q_e is the adsorption capacity, and Q_m is the saturated adsorption amount [4]. The linear diagram obtained according to the calculation is shown in Figure 6b. According to the calculation, the maximum adsorption capacity of FeS/LDH for Cr(T) and Cr(VI) was 102.9 mg/g and 147.7 mg/g, respectively. Compared with other, similar materials reported in the literature (Table 1), the removal efficiency of FeS/LDH outperforms other modified/unmodified LDH materials. In analogy to hydrotalcite materials, Cr removal could be facilitated after modification by improving the redox properties of its chelating ability. The same explanation can be applied to FeS/LDH in this study.

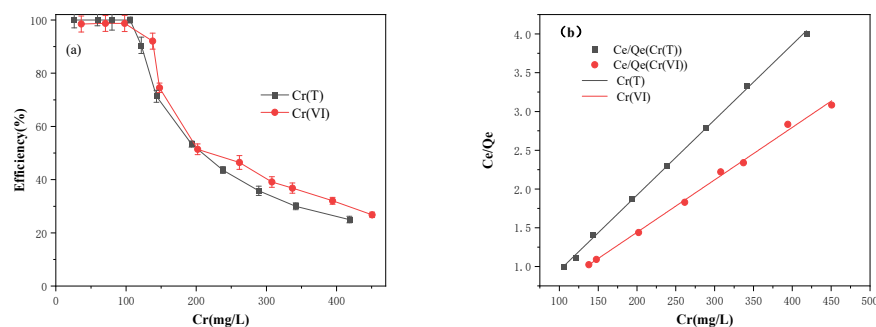


Figure 6. Effect of Cr concentration on the removal efficiency of FeS/LDH3 (a) and corresponding Langmuir adsorption fitting (b).

Table 1. Performance comparison of different adsorbents for Cr(T) and Cr(VI) removal from aqueous solution.

Adsorbents	Q_m (Cr(T), mg/g)	Q_m (Cr(VI), mg/g)	References
Sand/MgAl LDH		29.9	Chengguang Gao [27]
S-Mg LDH		47.9	Shuang Xu [28]
S-Ca LDH		56.2	Shuang Xu [28]
Fe ₃ O ₄ -ZnAl LDH		47.3	Yanting Yang [29]
EDTA@MgAl LDH	38.0		Danlian Huang [47]
MgAl-MoS ₄ LDH		130.0	Lijiao Ma [30]
MgAlFe-MoS ₄ LDH		135.6	Gebremedhin G. Aregay [48]
LDHNSs		126.0	Bo Zhang [49]
FeS/LDH3	102.9	147.7	This article

3.3. Removal Mechanisms

To further explore the detailed adsorption mechanism of FeS/LDH on Cr, FeS/LDH3 before and after adsorption was analyzed by XPS as shown in Figure 7. After Cr(VI) adsorption, new peaks are observed for Cr 2p in Figure 7a. The Fe 2p spectrum (Figure 7b) showed that the relative peak area ratio of Fe²⁺ decreased while the peak area ratio of Fe³⁺ increased [4]. In the energy spectrum of S 2p (Figure 7c), the original characteristic peak area ratio changed, where the peak area of S²⁻ (69.33%), SO₃²⁻ (0.94%) and SO₄²⁻ (29.73%) became S²⁻ (1.05%) and SO₃²⁻ (53.07%) and SO₄²⁻ (45.87%) after adsorption of Cr [40]. This observation confirmed that the oxidation reaction occurred during Cr adsorption, where FeS acted as reducing agent. In the Cr 2p spectrum of FeS/LDH3 after adsorption (Figure 7d), there were peaks at 576.1 eV, 577.2 eV, and 586.6 eV that can be assigned to Cr(III), which were not consistent with the characteristic peaks of the raw material K₂Cr₂O₇ in the file [29]. This indicated that the main form of Cr in the reacted material is Cr(III) [40]. Obviously, the main Cr removal from the solution mechanism of FeS/LDH involves (1) anion exchange allowing Cr(VI) to enter the interlayered structure of LDH, (2) reduction of Cr(VI) to Cr(III) utilizing reductive properties of Fe²⁺ and S²⁻, and (3) Fe³⁺ and Cr³⁺ co-precipitation to remove Cr(T) [34,49]. The schematic diagram of the removal mechanism is shown in Figure 8. The method of adsorption–reduction adopted in this study reduced the toxicity and content of the Cr pollutant, achieving efficient treatment of Cr in aqueous solution.

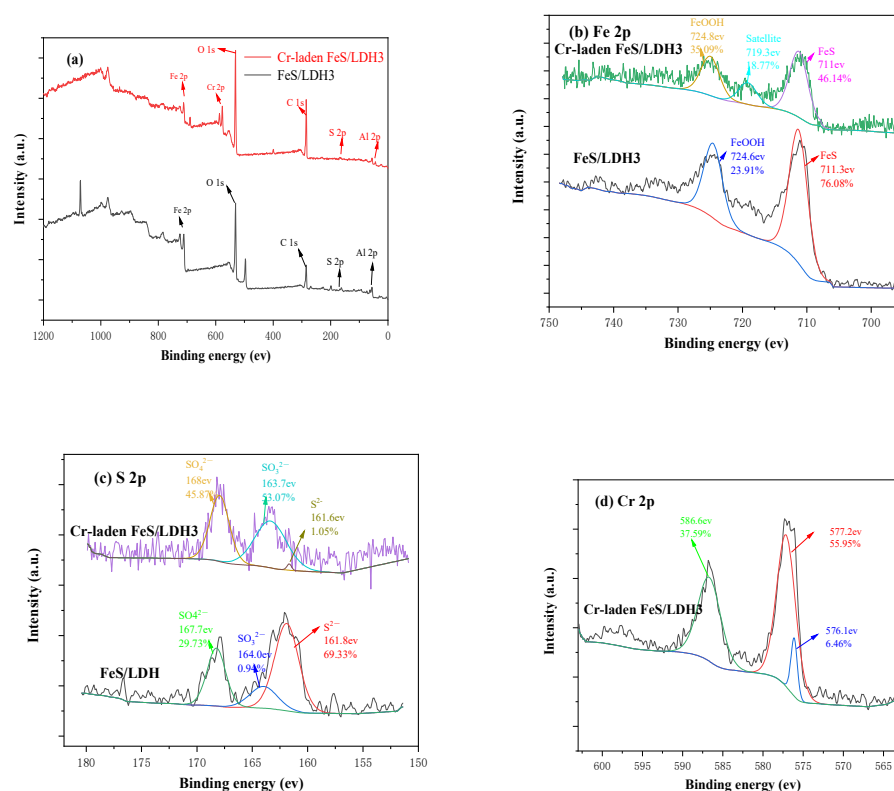


Figure 7. XPS full spectrum (a), Fe 2p (b), S 2p (c) spectra of pure FeS/LDH3 and Cr-laden FeS/LDH3, and Cr 2p (d) spectrum of FeS/LDH3.

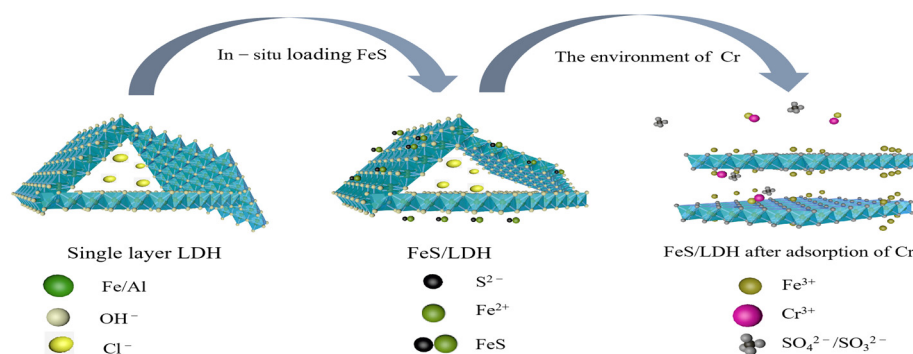


Figure 8. Schematic diagram of removal mechanism.

4. Conclusions

This paper reports that FeS was successfully incorporated between the layers of Fe-Al LDH by precipitation method to produce FeS/LDH composite material. It provides a new type of reducing agent for removing Cr in water. The experimental results show that the material exhibits superior Cr removal performance. A variety of factors that could affect Cr adsorption, including the ratio of Fe and Al, initial pH, FeS, coexisting anions and Cr concentration were tested. At the initial Cr concentration of 100.0 mg/L and initial pH value of 3.0, a removal efficiency of 99.5% for Cr(T) and Cr(VI) was achieved. The maximum adsorption capacity of Cr(T) was 102.9 mg/g, and the maximum adsorption capacity of Cr(VI) was 147.7 mg/g. The good Cr removal performance was mainly attributed to the triple synergistic effect of anion exchange, double reduction, and co-precipitation. The composite material also showed improved resistance to influence by common coexisting anions in the environment. Therefore, further research on the material in actual wastewater or soil can be carried out in the future.

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