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# Study on the synthesis of modified materials and their adsorption performance on heavy metal ions from aqueous solution

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Abstract. In this work, the schwertmannite modified by different divalent cations were successfully prepared and used for the adsorption of Cr(VI) and Cu(II) from aqueous solutions. The characterization was measured by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier Transform infrared spectroscopy (FTIR). FTIR results show that the doping of Mg<sup>2+</sup> and Mn<sup>2+</sup> significantly increased the content of hydroxyl group. Moreover, the adsorption kinetic study illustrated that chemisorption mainly controlled the Cr(VI) and Cu(II) removal process. Therefore, schwertmannite modified by doping with divalent cations could be a potential adsorbent for the remediation of Cr(VI) and Cu(II) containing wastewater.

#### 1. Introduction

Heavy metals pollution origin from many industrial processes such as mining exploitation, machinery processing, metal smelting, and surface treatment [1], is a one of the most serious environmental problems that needed to resolve worldwide. The pollution caused by the heavy metals may result in long-term chronic toxicity to the environment and human body through multiple pathways. The removal of heavy metals from aqueous solution is essential, and numerous techniques have been proposed.

So far, many technologies have been employed in the treatment of heavy metal contaminated wastewater, such as coagulation-flocculation, membrane processing, chemical precipitation, ion exchange, adsorption [2]. However, with the disadvantage of higher cost, selectivity imperfections and lower efficiency existed in those methods mentioned previously limited their practical application. Using activated carbon, biochar, biomass, hydrous metal oxides, etc. as heavy meatal adsorbent has been proven to be effective, eco-friendly, and low-cost [3]. The adsorbent provided ion exchange sites, surface complexation or lattice vacancy for metal ions removal. A desired adsorbent should have stable mechanical structure, high adsorption capacity and economic. Iron sulfate hydroxide mediated by acidophilic bacteria has gained increasing attention in geological and environmental area.

The schwertmannite  $(Fe_8O_8(OH)_{8-2x}(SO_4)_x)$ , one kind of iron hydroxy sulfates, is well known for its high specific surface area, low crystallinity, surface reaction activity, and tunnel structure, which played

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an critical role in dominating the fate and transport of various contaminants [4, 5]. In the acid mine drainage environment with high concentration of iron and sulfate, the schwertmannite can be biosynthesized by chemoautotrophic acidophilic bacteria. The inorganic elements can be migrated, enriched, transformed and formed secondary minerals under the precise regulation of bacteria surface group or by its metabolites. Biosynthesis method as an effective, sustainable and low-cost choice for iron-based materials synthesis attracted more and more interests over the years [6].

Schwertmannite synthesized by chemical or biological methods were typically presented in micronsized spherical aggregates form. However, the inner reactive area would be sheltered due to the spherical structure. Its specific surface area would be diminished and adsorption capacity would be weakened at the same time. Researchers found that cationic doping significantly changes the composite, surface properties, particle size and structure of the material [6].

Herein, the objective of this work is to synthesize the divalent ion-modified schwertmannite for efficient removal of Cr(VI) and Cu(II) from aqueous solution. The prepared materials were characterized and analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Furthermore, in order to further study the adsorption behavior of modified schwertmannite materials on Cr(VI) and Cu(II), the adsorption time were investigate and the adsorption kinetic model was established.

# 2. Materials and methods

# 2.1. Bacteria domestication and culture expansion

The strains used in this study were *A. ferrooxidans* 23270. The 9K medium was diluted once and adjusted to pH 2.0, then dispensed to 500 mL Erlenmeyer flask. The medium volume was 250 mL and sterilized at 121 ° C for 20 min. *A. ferrooxidans* 23270 was inoculated into medium in a volume of 5%. 11.17 g of FeSO<sub>4</sub>·7H<sub>2</sub>O was added into 250 mL system, and the culture was accelerated until it reached a stable Fe(II) oxidation rate. The bacterium was domesticated in the same conditions for large scale culture. The growth cycle of bacteria was detected, and the precipitation removed through the filter from bacteria liquid. The collected bacteria were used to synthesis materials.

# 2.2. Material synthesis

Schwertmannite synthesis was conduct in 500 mL with 200mL solution system, and the base concentration of FeSO<sub>4</sub>.7H<sub>2</sub>O was prepared by adding 15 g of FeSO<sub>4</sub>.7H<sub>2</sub>O into 200 mL aqueous solution condition. There were five cations prepared to doping with, including  $Mn^{2+}$  and  $Mg^{2+}$  and each doping cation was set in two concentration. The dopant amount of MnSO<sub>4</sub> and MgSO<sub>4</sub> doping concentration was 15 g or 30 g. The synthesized corresponding schwertmannite was marked as Mn15, Mn30, Mg15 and Mg30, respectively. The initial pH of the synthesis system was adjusted to 2.5, and the collected bacteria were inoculated. The synthesis proceeds in 30°C and 170 rpm for 7 days. After completion of the synthesis, the material was collected by filter paper, and the precipitate was washed several times with deionized water at pH 2.0 and dried in room temperature.

# 2.3. Material characterization

Scanning electron microscopy (SEM) was performed by using a JSM-6360LV scanning electron microscope at a 15 kV accelerating voltage. XRD analysis was carried out by means of a Japanese RINT2000 powder diffraction spectrometer (Cu K $\alpha$  target, 40 kV / 250 mA) with a scanning range of 5° to 80° and a step size of 0.02°. The infrared spectrum was performed on a Nicolet Nexus Model 670 infrared analyzer with a resolution of 4 cm<sup>-1</sup> and a background of KBr.

# 2.4. Adsorption experiment

The Cu(II) and Cr(VI) adsorption experiment was conducted in 50 mL centrifuge tubes. 0.1 g of adsorbent was added into 10 mL 0.01 M NaNO<sub>3</sub> background electrolyte, and then the solution pH was adjusted with 5% HNO<sub>3</sub>. After the solution pH reached a stable level, another 10 mL 500 mg/L Cu(II)

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(copper nitrate) and Cr(VI) (potassium dichromate) at pH 3.0–8.0 were added into the adsorption system. The adsorption isotherm experiments were conducted with the following concentration of Cu(II) and Cr(VI) 30, 80, 150, 250 and 350 mg/L. The Cr(VI) concentration was determined calorimetrically using a diphenyl carbazide reagent. ALL of adsorption experiments were conducted in duplicate.

# 2.5. Kinetic study

Pseudo-first-order and pseudo-second-order models were employed to evaluate the kinetic data of Cr(VI) on the PR composites, and equations are shown in Eqs. (1) and (2), respectively.

$$\log(q_{e} - q_{t}) = \log q_{e} - \frac{\kappa_{1}}{2.303}t$$
(1)
$$\frac{t}{q_{t}} = \frac{1}{\kappa_{2}q_{e}^{2}} + \frac{1}{q}t$$
(2)

where  $q_e$  and  $q_t$  (mg/g) are the amounts of adsorbed Cr(VI) at equilibrium and at time t, respectively, and  $k_1$  and  $k_2$  are the pseudo-first-order and pseudo-second-order rate constants, respectively.

# 3. Result and discussion

# 3.1. Characterizations of prepared adsorbents



Fig. 1 Morphology of the schwertmannite synthesized with the different contents of divalent cations, (a) original synthesized schwertmannite; (b) Mg 15; (c) Mg 30; (d) Mn 15; (e) Mn 30.

Fig. 1 shows the morphology changes of schwertmannite minerals after doping with divalent cations. It can be observed (Fig. 1 (a)) that the original synthesized schwertmannite was presented as pom-pom aggregates with nano-scale needle-like structures on its surface. Once divalent cations were introduced, obvious changes on the morphology can be seen. In the case of Mg/Mn and Fe ratio is 1:1, the formed iron-based material still were spherical aggregates, but its fluffy structure disappeared and irregular surface protrusions were formed. When the ratio of Mg/Mn and Fe was 2:1, the spherical aggregates basically disappeared and flocculent structures were formed. We speculated that this transformation will greatly increase the specific surface area of the material. Consequently, the doping is effective and doping ions can control the morphology of schwertmannite.



Fig. 2 XRD patterns (a) and FTIR spectra of the synthesized schwertmannite (b).

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As indicated in the XRD patterns (Fig. 2 (a)), Mn and Mg show completely different conditions to the schwertmannite. After doping, the phase composition of schwertmannite did not change. There is no single, sharp, strong, distinguishable characteristic peak in the XRD pattern, which shows that the synthesized iron-based materials are still cast minerals in an amorphous state. Divalent cations have a significant morphological control effect on minerals, but they have not changed their phase and crystallinity.

Fig. 2 (b) indicates that Mg and Mn have different effects on the content of surface groups of schwertmannit. Compared to Mg ion, both ratios of Mn/Fe including 1:1 and 2:1 (Mn15 and Mn30) can significantly increase the hydroxyl content, which is indispensable to the proton exchange between the metal cation and the proton. Herein, though Mg and Mn are the same valence, they showed different effects on iron-based mineral groups.

# 3.2. Cr(VI) and Cu(II) adsorption kinetic study

The Cr(VI) and Cu(II) adsorption kinetics by prepared schwertmannite was investigated by the pseudo-first-order and pseudo-second-order fit models (Fig. 3 (a-b)). Obviously, all modified schwertmannite have higher adsorption capacity for Cr(VI) and Cu(II) than raw schwertmannite, indicating that the addition of  $Mg^{2+}$  and  $Mn^{2+}$  enhanced the adsorption capacity of schwertmannite. For Cr(VI) adsorption by schwertmannite, the removal performance was followed the order of Mg15 > Mn 15 > Mn 30 > Mg30 > Sh. For Cu(II) removal, the removal performance was listed as Mg15 > Mg30 > Mn15 > Mn30 > Sh.



Fig. 3 The pseudo-first-order fit and pseudo-second-order fit of Cr(VI) (a) and Cu(II) (b) adsorption by as-obtained schwertmannite.

Table 1 and 2 presented the kinetic parameters for Cr(VI) and Cu(II) uptake of prepared schwertmannite. Apparently, the pseudo-second-order model described all adsorption data well with higher  $R^2$  values, suggesting that chemisorption mainly controlled the Cr(VI) and Cu(II) removal process [7].

Table 1 Kinetic parameters for Cr(	VI) upta	ake of prepa	red schwertn	nannite
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	pseudo-first-order kinetics			pseudo-second-order kinetics		
adsorben ts	q <sub>e</sub> (mg/L)	k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/L)	$\begin{array}{c} k_2\\ (g\bullet mg^{-1}\bullet min^{-1})\end{array}$	R <sup>2</sup>
Sh	47.28	1.5736	0.6612	47.81	0.1548	0.9167
Mn15	58.47	2.4206	0.5990	59.09	0.1378	0.8905
Mn30	55.26	1.5780	0.6180	56.60	0.0559	0.9033

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Mg15	60.92	2.3165	0.5870	61.65	0.1173	0.8782
Mg30	54.89	1.5736	0.6458	56.19	0.0570	0.9189

Table 2 Kinetic parameters for Cu(II) uptake of prepared schwertmannite							
	pseudo-first-order kinetics			pseudo-second-order kinetics			
adsorben ts	q <sub>e</sub> (mg/L)	k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/L)	$\begin{array}{c} k_2\\ (g\bullet mg^{-1}\bullet min^{-1})\end{array}$	R <sup>2</sup>	
Sh	38.71	1.8704	0.5848	39.45	0.1105	0.8825	
Mn15	44.78	2.2224	0.7180	45.29	0.1555	0.9362	
Mn30	43.97	44.43	0.8361	44.43	0.1598	0.9695	
Mg15	50.43	1.5043	0.6029	51.75	0.0558	0.8715	
Mg30	46.69	1.7728	0.7977	47.47	0.0928	0.9781	

# 4. Conclusions

In this work, the schwertmannite modified by different divalent cations were successfully prepared and used for the adsorption of Cr(VI) and Cu(II). All modified schwertmannite have higher adsorption capacity for Cr(VI) and Cu(II) than raw schwertmannite. All of our results indicated that schwertmannite modified by doping with divalent cations is a promising adsorbent for the remediation of heavy metal polluted water.

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