



Research paper

Calcined Mg/Al-LDH for acidic wastewater treatment: Simultaneous neutralization and contaminant removal

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ABSTRACT

Acid drainage (AD) poses a significant concern for water pollution due to its strong acidity and the toxicity of its various contaminants (e.g., heavy metal ions). In order to minimize the harmful effects of AD, the acidity must be neutralized and the contaminants be removed. The capacity of calcined Mg/Al layered double hydroxide (Mg/Al-CLDH) for simultaneously neutralizing the pH of AD and removing various heavy metal cations and oxyanions (Cr(VI) and phosphate) was studied herein. The interactions throughout co-removal between metal cations (in short M) and oxyanions were particularly investigated. In the solution with only M, Mg/Al-CLDH was capable of neutralizing solution pH and removing M. The reconstruction of LDH from Mg/Al-CLDH produced OH⁻ to neutralize pH and partially remove M through precipitation. FT-IR results suggested that forming H-bonds with the reconstructed LDH (R-LDH) might also contribute to M removal. In the solution containing both M and oxyanions, M and oxyanions could mutually affect their removal efficiency by Mg/Al-CLDH. M weakened the removal capacities of Cr(VI) and phosphate, because it could compete for adsorption sites on R-LDH. Cr(VI) and phosphate showed complex effects on the removal of M: Low concentrations of Cr(VI) promoted the removal of M by providing extra adsorption sites; high concentrations of Cr(VI), however, had the opposite effect, as a high concentration of Cr(VI) might largely occupy the adsorption sites on R-LDH. By contrast, phosphate inhibited the removal of M considerably, which might be ascribed to its strong buffering ability that maintained a relatively strong acidic nature of the solution. Our results, for the first time, showed that Mg/Al-CLDH is particularly suitable for the treatment of AD containing various contaminants.

1. Introduction

Acid drainage (AD) from mine and some industrial manufactories (e.g., batteries, tanneries, electrical, and electroplating factories) (Nguyen et al., 2013), is one of the most obnoxious environmental challenges worldwide. AD continues to contribute to water pollution due to its strong acidity, with pH values being as low as 2 (Feng et al., 2004), as well as toxicity caused by a diversity of contaminants, particularly heavy metal cations and oxyanions (e.g., cobalt, nickel, cadmium, copper, lead, zinc, chromate (Cr(VI)), and phosphate) (Sheoran and Sheoran, 2006). Considering the detrimental effect on aquatic plants, wildlife, and even ground water (Feng et al., 2004), the discharge of untreated acid waters into public streams should be strictly prohibited. Various methods currently exist for the treatment of AD,

such as ion exchange, reverse osmosis, adsorption, and precipitation, (Feng et al., 2000; Kefeni et al., 2017; Li et al., 2008). The methods of ion exchange, reverse osmosis, and adsorption are useful for the removal of toxic contaminants, but generally show little efficacy in pH neutralization. The approach of precipitation favors the removal of toxic heavy metal cations as well as the consumption of H⁺, but generally is not efficient in removing anionic contaminants at their relatively low concentrations. Moreover, in order to precipitate metal cations the liquid pH must be increased to a high value according to the K_{sp} of their hydroxides, sometimes upwards of 9.7 (Table S1, supplementary information). Therefore, the most desirable materials for the treatment of AD would be able to simultaneously remove heavy metal cations and anions while neutralizing solution pH.

Layered double hydroxides (LDH), a type of anionic clay, have

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positively charged metal hydroxide sheets with anions located interstitially. One of their interesting characteristics is that their calcined products (CLDH), also known as double metal oxides, can rehydrate and recover to LDH (named as R-LDH) in aqueous environment (Eiby et al., 2016; Miyata, 1980). In this process, double oxides capture hydrogen atoms from water, thereby leaving OH^- to increase the pH of the liquid. CLDH also show high performance as adsorbents for removing various anionic contaminants (Ahmed and Gasser, 2012; Zaghouane-Boudiaf et al., 2012; Zhang et al., 2014; Zhu et al., 2005), but their use in cation removal initially has not been considered due to the positive charge on the nanosheets of R-LDH and the strong affinity of CLDH toward anions. Recent report, however, found that CLDH could effectively remove some cationic contaminants as well (Sun et al., 2015). Given that, we expect that CLDH can be a promising candidate for the treatment of AD, i.e., simultaneously removing cationic and anionic contaminants and neutralizing solution pH.

However, due to the strong affinity that CLDH exhibit toward anions, and anionic and cationic contaminants always coexist in wastewater, it is important to verify whether the existence of anionic contaminants will affect the removal of heavy metal cations when using CLDH as remover. On the other hand, CLDH have been substantiated as excellent adsorbents for anionic contaminants in single contaminant system in numerous studies (Ahmed and Gasser, 2012; Zaghouane-Boudiaf et al., 2012; Zhang et al., 2014; Zhu et al., 2005); it is also of interest to determine whether heavy metal cations will influence the removal of anionic contaminants.

In this work, the removal ability of Mg/Al-CLDH toward various divalent heavy metal cations (Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}) was first investigated in solutions of single metal cation, as well as in solutions of multiple coexisting metal cations. We changed the added amount of Mg/Al-CLDH, aiming to neutralize the acidity of AD while LDH was reconstructed from CLDH and also to control the adsorption of heavy metal cations. In order to distinguish the removal caused by adsorption on Mg/Al-CLDH from that caused by formation of aqueous precipitates (because of the increase of solution pH), the aqueous precipitation experiment was carried out for comparison. Additionally, the interplay between heavy metal cations and selected anionic contaminants (Cr(VI) and phosphate) in the co-removal system was investigated. The objective of this study is to verify whether CLDH are applicable of neutralizing the acidity of AD and removing heavy metal cations, and whether the coexisted heavy metal cations and anions will mutually affect their removal. This work devotes to explore the multifunction of CLDH to meet the various processing requirements for acidic wastewater.

2. Experimental details

2.1. Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, NaH_2PO_4 , NaOH , and HNO_3 with the purity over 98.0% were purchased from Guangzhou chemical reagent CO., LTD (Guangzhou, China). Ammonium molybdate (99.9%) and Ascorbic acid (99.99%) were purchased from Aladdin-E. Mg/Al-LDH (99.0%, molar ratio of Mg/Al = 2) with CO_3^{2-} located in the interlayers of its structure (XRD, BET data, and SEM image are shown in Fig. S1) was purchased from Hunan Shaoyang Tiantang Auxiliaries Chemical CO., LTD (Hunan, China). XRD pattern shows that Mg/Al-LDH possesses well crystallinity with the characteristic reflections of LDH. Mg/Al-LDH has a BET specific surface area of $105.1 \text{ m}^2/\text{g}$, which is close to those of LDH reported in literature (Shao et al., 2011; Yang et al., 2014). All chemicals were used as received.

2.2. Preparation of Mg/Al-CLDH

Mg/Al-CLDH (XRD, BET data, and SEM image are shown in Fig. S1)

was obtained by heating Mg/Al-LDH at 500°C for 3 h. Under this temperature the interlayer carbonate of Mg/Al-LDH can be decomposed to near completion according to our previous results (Laipan et al., 2015). Mg/Al-CLDH has a large BET specific surface area of $222.6 \text{ m}^2/\text{g}$ and pore volume of $0.74 \text{ cm}^3/\text{g}$.

2.3. Removal of heavy metal cations

1 L stock solution containing six metal cations (Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}) was prepared using nitrate salts (1000 mg/L for each cation, pH 2.0). Notably, Visual MINTEQ (version 3.0) was employed to test whether the mixing of various metal ions (Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Mg^{2+} , and Al^{3+}) would generate undissolved substances (except metal hydroxides which caused by pH increase), such as minerals, under the experimental conditions. The simulation results indicated no other precipitate was generated. Batch adsorption experiments were carried out using a conical flask with cover (to avoid the adsorption of CO_2 from atmosphere) at 25°C on a shaker with a shaking speed of 200 rpm for 6 h. Initial solution pH was 2.0 and the concentration of each heavy metal cation was 20 mg/L . The adsorption studies were conducted by varying the initial amount of Mg/Al-CLDH added from $0.30\text{--}0.80 \text{ g/L}$. Concentrations of the six metal cations and the pH of the solutions were detected as time increases. Atomic Absorbance Spectrometer (PE Analyst 400) was utilized to determine the concentrations of the remnants metal cations. For comparison, simultaneous removal of these heavy metal cations through aqueous precipitation due to pH increase was conducted as well, with NaOH serving as a pH modifier. Meanwhile, the efficiency of Mg/Al-CLDH in the removal of each heavy metal cation in the single cation systems was also examined. All of the experiments were conducted in duplication.

2.4. Simultaneous removal of heavy metal cations and oxyanions

Five heavy metal cations, i.e., Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} , and two oxyanions, i.e., Cr(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$) and phosphate (NaH_2PO_4), were used to constitute the simulated AD system (As Pb^{2+} and Cr(VI) will form insoluble solid even at low solution pH, Pb^{2+} will not be discussed in this part). Similarly, Visual MINTEQ simulation results also indicated that the adding of Cr(VI) or phosphate would not produce precipitate under the experimental conditions. The experimental conditions, procedure, and heavy metal ions detection technology remained consistent with above description, with the exception of the concentrations of Cr(VI) ($20\text{--}200 \text{ mg/L}$, the mass concentrations of Cr; molar concentrations of 0.38 to 3.85 mmol/L) and phosphate ($20\text{--}200 \text{ mg/L}$, the mass concentrations of P; molar concentrations of 0.65 to 6.45 mmol/L). The concentration of phosphate in the supernatant was measured using the molybdenum method (Liu et al., 2016; Murphy and Riley, 1962). For comparison, removal isotherms of Cr(VI) and phosphate were also plotted under a single Cr(VI) or phosphate system, i.e., without the existence of heavy metal cations. All of the experiments were conducted in duplication.

2.5. Characterization methods

The rehydrated and recovered products of Mg/Al-CLDH under water rich in NO_3^- and solutions with various pollutants were collected and coated on the surface of cover glass. XRD patterns of these dried samples were measured on a Bruker D8 ADVANCE X-ray diffractometer using Cu K α radiation operating at 40 kV and 40 mA. The patterns were recorded over the 2θ range from 3 to 80° with a scan speed of $3^\circ/\text{min}$ using a bracket sample holder. The slit width is 0.6 mm .

The dried rehydrated and recovered products of Mg/Al-CLDH under water rich in NO_3^- and solutions with various pollutants and KBr were first pressed to disks. The disks were prepared by pressing a mixture of 0.9 mg powdered sample and 80 mg KBr. And then the Fourier

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