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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

$Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $K_2Cr_2O_7$, 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 ration 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 patter 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 m^2/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 m^2/g and pore volume of 0.74 cm^3/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 0.30–0.80 g/L. Concentrations of the six metal cations and the pH of the solutions were detected as time increases. Atomic Absorbance Spectrometer (PE AAnalyst 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) (K_2Cr_2O7) 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) (20–200 mg/L, the mass concentrations of Cr; molar concentrations of 0.38 to 3.85 mmol/L) and phosphate (20–200 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 Kα 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°/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

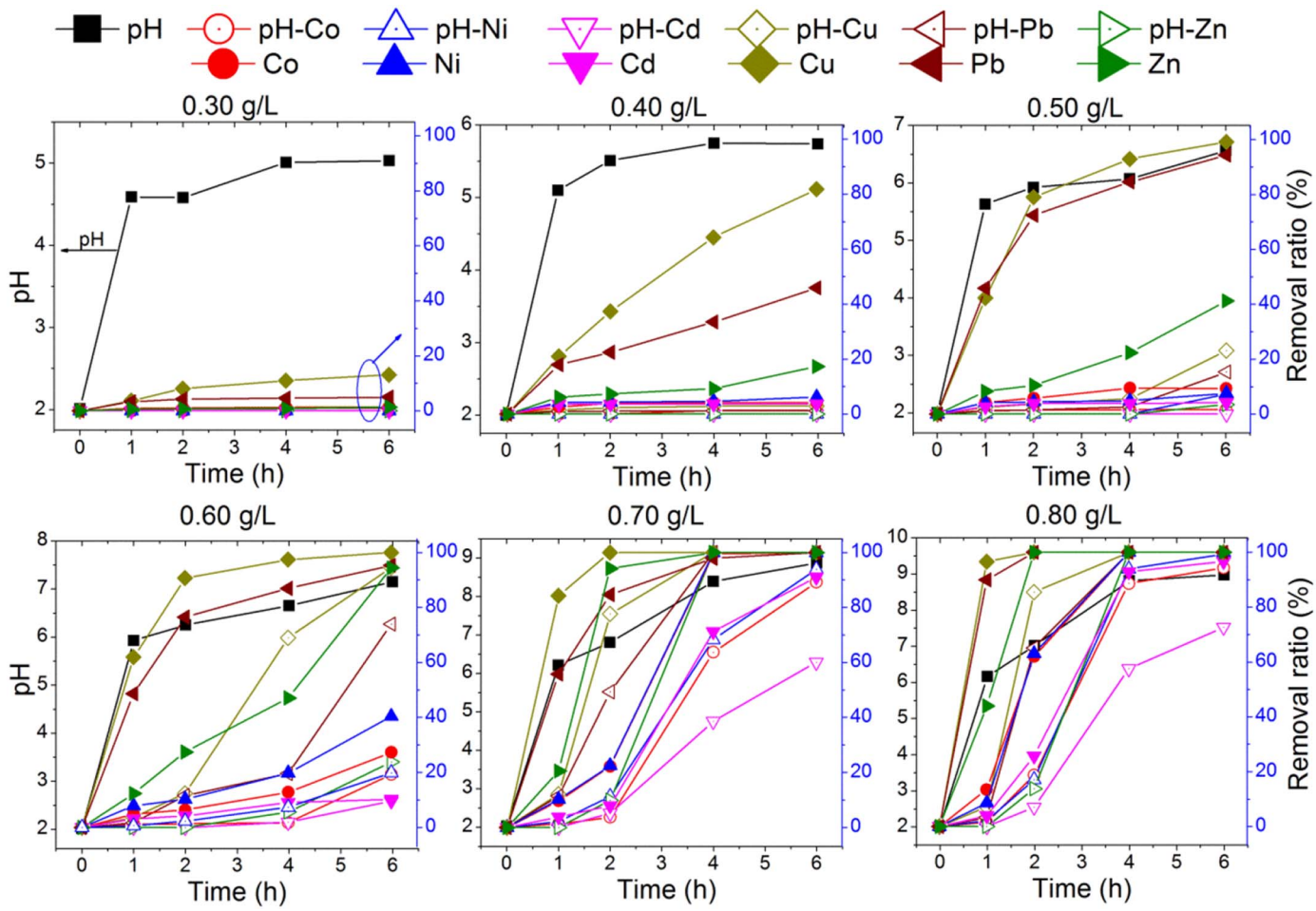

Fig. 1. Simultaneous removal efficiencies of Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} by Mg/Al-CLDH with different adding amounts (g/L); pH-Co, pH-Ni, pH-Cd, pH-Cu, pH-Pb, and pH-Zn represent the removal efficiency of precipitation caused by pH increase using NaOH as the modifier (concentration for each metal cation is 20 mg/L; all of the data are average values of the two paralleled tests).

Transform Infrared (FT-IR) spectra were obtained using a Bruker VERTEX 70 spectrometer. All spectra were recorded at room temperature over the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

3. Results and discussion

3.1. Removal efficiency of six heavy metal cations

The experimental results showed that as the concentration of Mg/Al-CLDH was increased from 0.30 to 0.80 g/L, the simultaneous removal ratios of all the heavy metal cations were increased to approximately 100% (Fig. 1, the detailed data is shown in Table S2). The removal of heavy metal cations was not solely influenced by precipitation, but also by adsorption on Mg/Al-CLDH, since the removal efficiency of Mg/Al-CLDH was much higher compared to that caused by precipitation using NaOH as the pH modifier. Notably, the curves of the precipitation of heavy metal ions vs. pH condition caused by NaOH showed differences to those of the simulated values by Visual MINTEQ (Fig. S2). The precipitation results in this study showed lower precipitation efficiencies for the heavy metal cations (except Co^{2+} and Cd^{2+}) than those of the simulated values at the same pH value. Apart from the influence of experimental process (e.g., the measure errors), the above differences might also be caused by the parameters used in simulation, as the metal hydroxides may have different *Ksp* at room temperature. For example, it is reported that $Pb(OH)_2$ has several *K*sp values under room temperature, such as 1.43×10^{-15}, 1.43×10^{-20}, and 5.01×10^{-16} (Arce et al., 2015; Liu and Liu, 2003).

The results of this work showed that using Mg/Al-CLDH for the removal of heavy metal cations in AD offered several advantages. First, Mg/Al-CLDH demonstrated a significantly higher rate of efficiency in the simultaneous removal of various heavy metal cations in simulated AD than that of the precipitation caused by NaOH. In addition, the pH of AD could be adjusted by changing the added amount of Mg/Al-CLDH, and appropriate amount of Mg/Al-CLDH (e.g., 0.60–0.70 g/L) could achieve the removal of almost all of the heavy metal cations without raising the pH of AD too high (e.g., pH $<$ 8.4). Furthermore, Mg/Al-CLDH exhibited different removal selectivity toward certain heavy metal cations, showing much higher affinity to Cu^{2+}, Pb^{2+}, and Zn^{2+} than to the other three metal cations. The selectivity presented in an order of $Cu^{2+} > Pb^{2+} > Zn^{2+} \gg Co^{2+}, Ni^{2+} > Cd^{2+}$.

The results of the removal of individual heavy metal cations in single cation systems also showed that Mg/Al-CLDH exhibits high removal efficiency and pH neutralization property (Table S3). The removal capacity was actually enhanced in the single metal cation system as compared in the mixture system (with various heavy metal cations), probably because of the absence of competitive adsorption and higher final solution pH of the single metal cation system than that of the mixture system.

3.2. Removal efficiency of both cations and oxyanions

The behavior of cation removal was first verified in the simulated AD system with the co-existence of Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+},

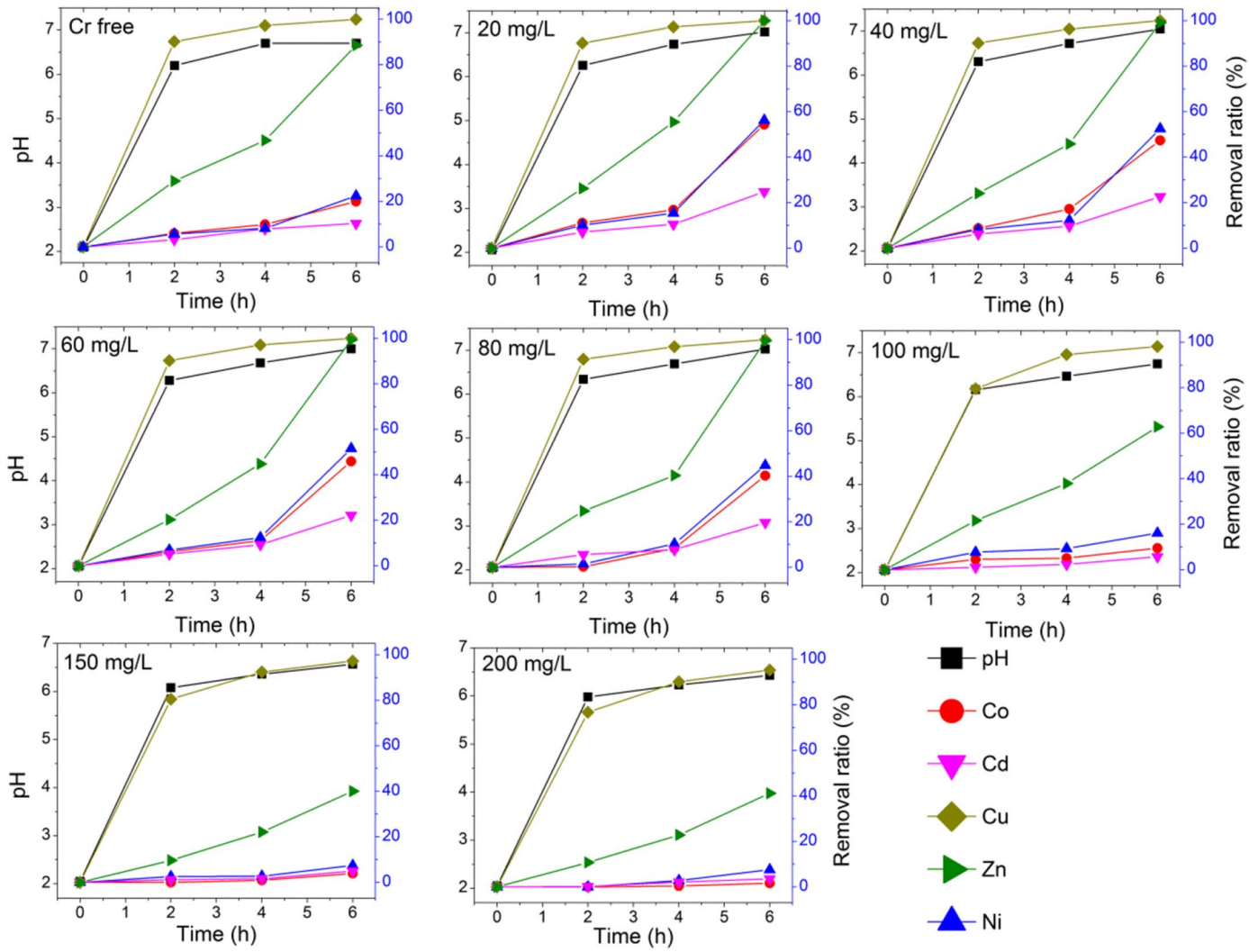

Fig. 2. Simultaneous removal efficiencies (average values of the two paralleled tests) of Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} by Mg/Al-CLDH (0.50 g/L) under the co-existence of Cr(VI) with different concentrations. (Concentration for each metal cation is 20 mg/L and those for Cr(VI) vary from 20 to 200 mg/L).

and Cr(VI). In these experiments, the added amount of Mg/Al-CLDH was of 0.50 g/L. The removal efficiencies for these heavy metal cations decreased with increasing Cr(VI) concentration (Fig. 2, the detailed data is shown in Table S4); but an interesting finding was that the removal was enhanced in solutions with relatively low Cr(VI) concentrations (≤ 80 mg/L) compared to solution without Cr(VI) (Table S5). On the other hand, the presence of phosphate greatly suppressed the removal of cations (in the solution containing both heavy metal cations and phosphate), and the increase of phosphate concentration caused a pronounced decrease of heavy metal cations removal efficiency (Fig. 3, the detailed data is shown in Table S6).

Similarly, the presence of heavy metal cations also affected the removal of Cr(VI) and phosphate (Fig. 4). The removal of Cr(VI) was obviously inhibited by metal cations, with sharp differences in the maximum amount of adsorbed Cr(VI) under each equilibrium concentration. In contrast, the existence of heavy metal cations exerted less influence over the removal of phosphate than Cr(VI), as the amount of removed phosphate decreased only slightly at the equilibrium concentrations.

3.3. The possible removal mechanism for heavy metal cations

The reconstruction of LDH from CLDH is a process that double metal oxides recover to double metal hydroxide structure while generation of hydroxides (Miyata, 1980). The calcination of LDH and reconstruction of LDH from CLDH can be shortly described by Eqs. (1) and (2) (Extremera et al., 2012):

$$Mg_2Al(OH)_6(CO_3)_{0.5} \rightarrow Mg_2AlO_{3.5} + 3H_2O + 0.5CO_2 \tag{1}$$

$$Mg_2AlO_{3.5} + 3.5H_2O + NO_3^- \rightarrow Mg_2Al(OH)_6(NO_3^-) + OH^- \tag{2}$$

However, before and during LDH formation some reactions, such as hydrolysis and dissolution of MgO and Al_2O_3 and dissociation of $Mg(OH)_2$ and $Al(OH)_3$, occur on the surface of the solid particles, simplified as follows (Xu and Lu, 2005):

$$MgO + H_2O \rightleftarrows Mg(OH)_2 \rightleftarrows Mg^{2+} + 2OH^- \tag{3}$$

$$MgO + 2H^+ \rightarrow Mg^{2+} + H_2O \tag{4}$$

$$Al_2O_3 + H_2O \rightleftarrows 2Al(OH)_3 \rightleftarrows 2Al(OH)_2^+ + 2OH^- \rightleftarrows 2Al(OH)^{2+} + 4OH^- \rightleftarrows 2Al^{3+} + 6OH^- \tag{5}$$

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \tag{6}$$

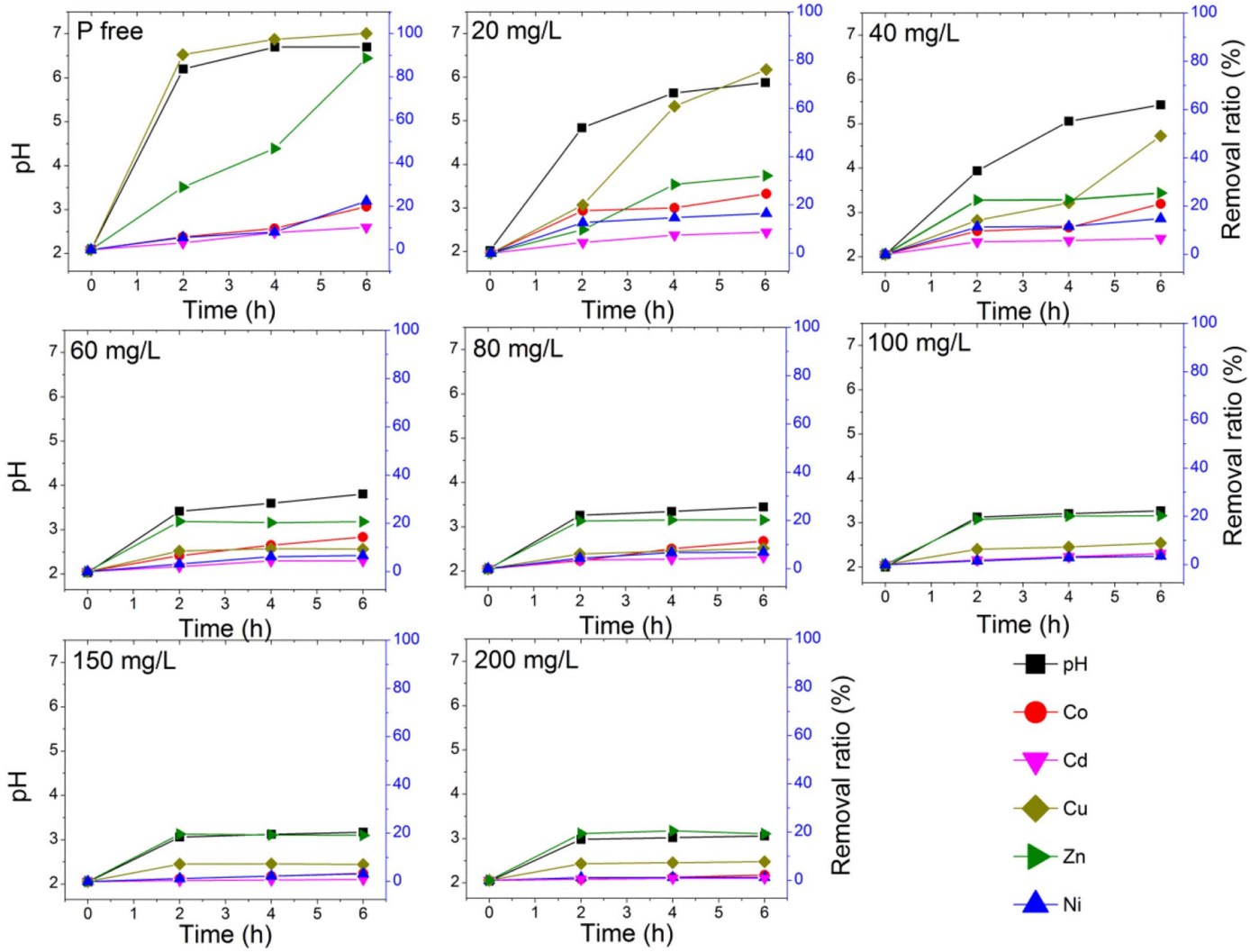

Fig. 3. Simultaneous removal efficiencies (average values of the two paralleled tests) of Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} by Mg/Al-CLDH (0.50 g/L) with the co-existence of phosphate. (Concentration for each metal cation is 20 mg/L and those for phosphate vary from 20 to 200 mg/L).

These equations (i.e., Eqs. (3)–(6)) offer an explanation for the low removal efficiencies of heavy metal cations under low addition amounts of Mg/Al-CLDH and low solution pH (Table S2). At low addition amounts of Mg/Al-CLDH which showed limitation to neutralize solution pH, the recovering of LDH structure was hindered indicated by XRD results (Fig. 5). The weak reconstruction of LDH structure should greatly be affected by the Eqs. (3)–(6). With the further increase of pH, Eq. (2) dominated the LDH recovering process, in which the removal of heavy metal cations was promoted. As divalent metal cations (M) commonly show hydrated forms in water, and M are Bronsted acid, the

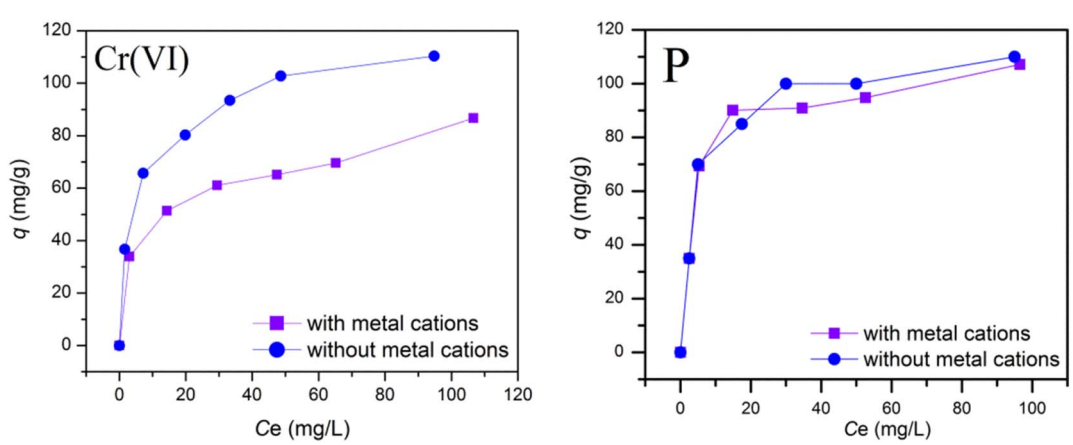

Fig. 4. Adsorption isotherms (average values of the two paralleled tests) of Cr(VI) and phosphate (P) by Mg/Al-CLDH (0.50 g/L) with and without the co-existence of heavy metal cations (Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}).

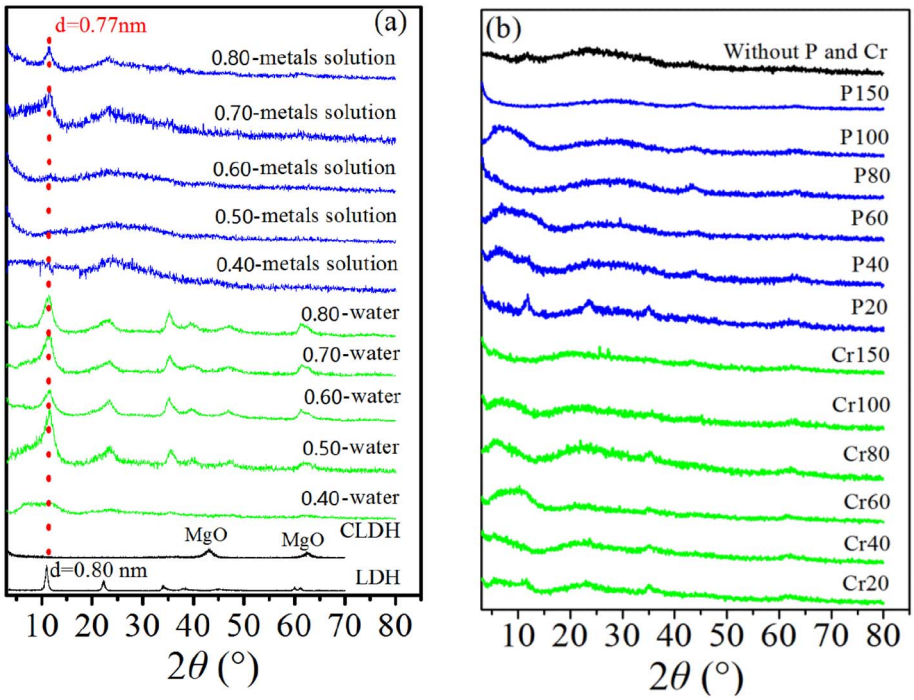

Fig. 5. XRD patterns of (a) reconstructed products of Mg/Al-CLDH with different adding amount of Mg/Al-CLDH (0.40–0.80 g/L) under heavy metal cations (nitrate) solutions and waters with same concentration of NO_3^- ($NaNO_3$), 0.40-water and 0.40-metals solution means adding 0.40 g Mg/Al-CLDH to 1 L water and metal solution, respectively; (b) reconstructed products of Mg/Al-CLDH (0.50 g/L) under the coexisting solution of heavy metal cations and anions (Cr(VI) or phosphate (P)). (Concentration for each metal cation is 20 mg/L and those for anions vary from 20 to 150 mg/L).

following equation exists in water (Brown and Ekberg, 2016):

$$[M(H_2O)_n]^{2+} \rightarrow H^+ + M(OH)^+ \quad (n = 1, 2, 3...) \tag{7}$$

The Eq. (2) will facilitate Eq. (7) going from left to right via the consumption of H^+; Eq. (7) will also favor the Eq. (2) in return. As a result, more $M(OH)^+$ will be generated, which will favor the removal of heavy metal cations by partly forming precipitates (Eq. 8) (Brown and Ekberg, 2016):

$$M(OH)^+ + OH^- \rightarrow M(OH)_2 \tag{8}$$

Though Eq. (8) can cause the removal of heavy metal cations, the results of this work showed that Eq. (8) (i.e., by precipitation) only partly contributed to the removal (Fig. 1). Therefore, other factors also gave rise to the removal. It was reported that when CLDH are rehydrated in metal cation solution, metal cation is able to participate in the reconstruction of LDH through isomorphous substitution with obvious changes in d(003) values of R-LDH (Sun et al., 2015). In this work, however, XRD patterns of the reconstructed LDH obtained in the mixture solution of various heavy metal cations indicated that there was no obvious changes of the d(003) values of these reconstructed LDH compared to those of the reconstructed products in water (Fig. 5a). But the variation in d(003) values may be quite small due to the small diameters of these heavy metal cations. According to the XRD refinement results of the two representative samples which reconstructed respectively in metal solution and NO_3^- involved water, the refined lattice parameter values of "a" showed difference with values respectively of 3.0537 and 3.0918 for the two samples (Table S7), which indicated the existence of isomorphous substitution of Mg^{2+} by other divalent heavy metal cations. Therefore, the replacement of Mg^{2+} by the divalent heavy metal cations also contributed to the removal of various heavy metal cations.

Previous reports showed that metal cations, particularly transition metals, could often play a considerable and varied role in hydrogen bonding (Brammer, 2003; Epstein and Shubina, 2002; Pehlivan et al., 2008; Shubina and Epstein, 1992; Wall et al., 1999). Brammer (2003) summarized that metal atoms and their complexes could be hydrogen bond acceptor or donor, forming various types of hydrogen bonds, such as Mt.-H…A, D-H…Mt., Mt.-D-H…A, and D-H…A-Mt. (where Mt., A, D, and … represent metal atom, hydrogen bond (proton) acceptor, hydrogen bond donor, and hydrogen bond, respectively), in a review paper. In certain instances, it was reported that the hydrated metal ions of Cd^{2+} and Cu^{2+} could form hydrogen bonds with glucose from mostly cellulose which caused the removal of Cd and Cu (Al-Ghouti et al., 2010; Pehlivan et al., 2008). Given that, FT-IR characterization was further conducted to detect hydrogen bonds to verify the removal mechanisms of heavy metal cations by CLDH.

FT-IR characterization results showed that with increasing the added amount of Mg/Al-CLDH (which consequently increased the removal ratios of heavy metal cations), the FT-IR peaks of O—H vibration shifted from 3468 to 3448 cm^{-1} (Fig. 6a). The red shift might be related to the formation of hydrogen bond (Mg(Al) − O − H···A) (A may be O in hydrated metal cations or $[OH\text{-}M]^+$, or even metal cations (Brammer, 2003)) which generally encourages an O—H bond elongation (Joseph and Jemmis, 2007). In this type of hydrogen bond, A causes the electron density to move from the O region to the O—H bond region; that is, the electron density in O—H bond region is increased and thus results in red shift of O—H vibration (Chocholoušová et al., 2004). On the other hand, the electron density in the Mg(Al)—OH bond region will decrease in the formation of H-bond, which then should cause a blue shift of the IR vibration peak of Mg(Al)-OH. FT-IR results confirmed the blue shift of the Mg(Al)—OH vibration peak from 618 (Kloprogge et al., 2004) to 667 cm^{-1}. The red shift of the out-of-plane O—H vibration (from 852 (Wypych et al., 2003) to 829 cm^{-1}) provided further support for the formation of hydrogen bonds. These three aspects collectively suggested the formation of hydrogen bonds with the surface hydroxyl group on R-LDH might be another reason for the removal of heavy metal cations.

3.4. Possible interaction mechanism between cations and oxyanions

When 0.50 g/L Mg/Al-CLDH ideally recovered to R-LDH, approximately 25.0–29.4 mmol/L of H^+ will be needed or 25.0–29.4 mmol/L of OH^- will be generated by Eq. 2. The maximum concentration of H^+ in water at pH 2.0 is of 10 mmol/L. Therefore, Mg/Al-CLDH will first accept H^+ from water (Eqs. 4 and 6) and other matters that can dominate H^+. Adding heavy metal cations and oxyanions (Cr(VI) and phosphate)

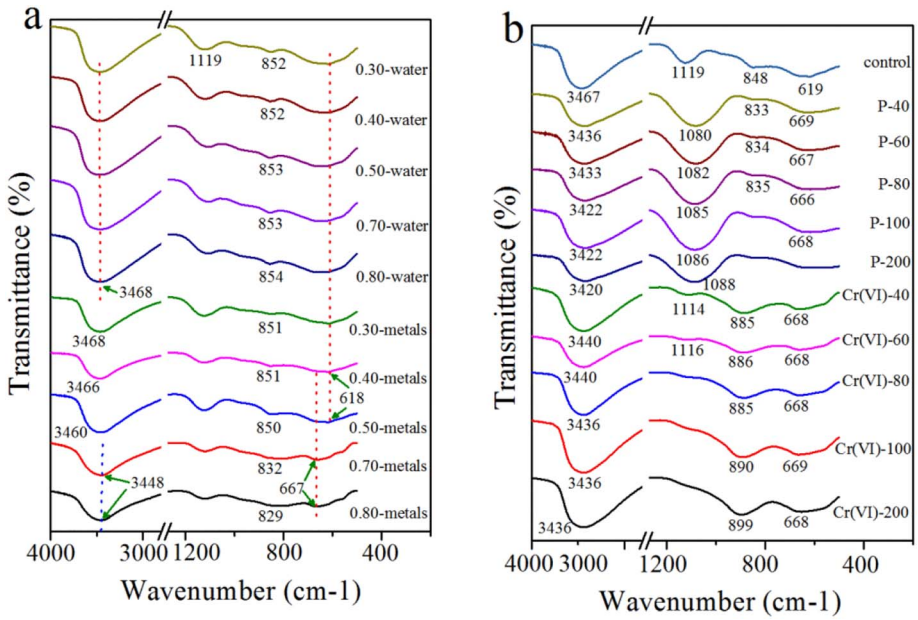

Fig. 6. FT-IR spectra of the products generated after contaminant removal in the heavy metal cations solution without (a) or with anionic pollutants (b). (0.30–0.80 represents the adding concentration (g/L) of Mg/Al-LDH in water or metal solution, and in (b) the concentration of Mg/Al-CLDH is 0.50 g/L; Concentrations for Cr(VI) and phosphate (P) vary from 40 to 200 mg/L).

certainly has impacts on the process of the reconstruction of LDH, which then will affect the removal of these contaminants in return.

When Mg/Al-CLDH rehydrated in heavy metal cations and Cr(VI) co-existing acidic solution, the Eqs. (9) to (11) would exist under the experimental conditions, in addition to Eqs. (2) to (8).

$$HCrO_4^- \rightarrow CrO_4^{2-} + H^+ \tag{9}$$

$$Mg_2AlO_{3.5} + HCrO_4^- + 2.5H_2O \rightarrow Mg_2Al(OH)_6(CrO_4)_{0.5} + 0.5CrO_4^{2-} \tag{10}$$

$$CrO_4^{2-} + [M(H_2O)_n]^{2+} \rightarrow HCrO_4^- + M(OH)^+ \tag{11}$$

At an initial stage, Cr(VI) mainly presented as $HCrO_4^-$; with the increase of solution pH caused by the rehydration of Mg/Al-CLDH, most $HCrO_4^-$ gradually transferred to CrO_4^{2-} (Barrera-Díaz et al., 2012). 20–200 mg/L of Cr(VI) can provide 0.38 to 3.85 mmol/L of H^+ through Eq. (9) when $HCrO_4^-$ completely transfers to CrO_4^{2-}. As such, Eq. (2) should dominate the rehydrating process. But Eqs. (9) to (11) also have their own effects to Eqs. (2) and (7) or the removal of heavy metal cations. Eq. (10) will weaken the rehydration of Mg/Al-CLDH via Eq. (2); but due to the co-contributions of Eqs. (2) and (10) the reconstruction of LDH was totally not affected (Fig. 5b). Eq. (9) inhibits Eq. (7) which reduces the formation of $M(OH)^+$, but Eq. (11) favor the formation of $M(OH)^+$ and Eq. (10) will favor Eq. (11) which ultimately promotes the formation of $M(OH)^+$. Thus, the formation of $M(OH)^+$ can be inhibited or promoted, which will further influence the removal of heavy metal cations.

FT-IR results provided new information on the interactions between both heavy metal cations and Cr(VI). Results showed that the adsorption of Cr(VI) on Mg/Al-CLDH (without the coexistence of heavy metal cations) caused red shift of (Mg/Al)O-H vibration from 3468 to 3436 cm^{-1} (Fig. S3), meaning that Cr(VI) was also able to form hydrogen bonds with the R-LDH. This means that Cr(VI) and heavy metal cations will compete for the adsorption sites (i.e., the surface hydroxyl) on the R-LDH. The competition for adsorption sites provides a reason for the fact that increasing Cr(VI) concentration resulted in decreasing removal efficiency of heavy metal cations, and adding heavy metal cations caused the decrease of the removal efficiency of Cr(VI). Conversely, the outcomes also showed that the adsorbed Cr(VI) could provide extra adsorption sites for heavy metal cations, as indicated by the differences in FT-IR results of $Cr^{VI}O_3$-stretch on the R-LDH rehydrated in Cr(VI) solutions with and without heavy metal cations. The vibration peaks of $Cr^{VI}O_3$-stretch at 882–924 cm^{-1} (Rapti et al., 2016) (Fig. S3) on the R-LDH rehydrated in Cr(VI) solutions shifted to 885–899 cm^{-1} (Fig. 6b) when added various heavy metal cations into the Cr(VI) solutions. This phenomenon provided a reason for the fact that adding proper amounts of Cr(VI) resulted in increasing removal efficiency of heavy metal cations.

When Mg/Al-CLDH rehydrated in heavy metal cations and phosphate co-existing acidic solution (phosphate mostly presents as $H_2PO_4^-$), the main Eqs. (12) to (15) would exist in addition to Eqs. (1), (2) and to (7),

$$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+ \tag{12}$$

$$Mg_2AlO_{3.5} + H_2PO_4^- + 2.5H_2O \rightarrow Mg_2Al(OH)_6(HPO_4)_{0.5} + 0.5HPO_4^{2-} \tag{13}$$

$$Mg_2AlO_{3.5} + HPO_4^{2-} + 2.5H_2O \rightarrow Mg_2Al(OH)_6(PO_4)_{1/3} + {}^{2}/_{3}PO_4^{3-} \tag{14}$$

$$H_2PO_4^- + [M(H_2O)_n]^{2+} \rightarrow H_3PO_4 + M(OH)^+ \tag{15}$$

20–200 mg/L of phosphate can provide 1.3 to 12.9 mmol/L of H^+ through Eq. (13) and (14). Therefore, Eqs. (3)–(6), (13), and (14) should dominate the rehydrating process of Mg/Al-CLDH. That is, the MgO and Al_2O_3 will first be badly dissolved and the reconstruction of LDH structures will be restrained confirmed by XRD results (Fig. 5). Therefore, the removal of heavy metal cations will be strongly inhibited. On the other hand, as $H_2PO_4^-$ mainly shows ionization in water (i.e., Eq. (12)) the reaction shown in Eq. (15) should be neglected. Also, Eqs. (2) and (7) would be badly inhibited. In this way, the formation of $M(OH)^+$ was greatly suppressed, which caused the pronounced decrease in removal efficiency of the heavy metal cations compared to that in the solution without phosphate (Fig. 3).

Phosphate and the R-LDH also formed hydrogen bonds, as indicated by the red shift of (Mg/Al)O-H vibration from 3467 to 3420 cm^{-1} and blue shift of Mg/Al-OH vibration from 619 to 668 cm^{-1} (Fig. 6b). Likewise, interactions between phosphate and heavy metal cations also existed, which could create adsorption sites for heavy metal cations, as the vibration peak of phosphate shifts from 1092 to 1082 cm^{-1}. Due to the acidity of the coexisting solution of heavy metal cations and

phosphate and the influence of Eq. (12) toward Eq. (7), however, the negative effect of phosphate to the removal of heavy metal cations overshadowed its positive effect, thereby caused sharp decreases to the removal efficiency for heavy metal cations. The decrease of adsorbed amount of heavy metal cations weakened the influence of heavy metal cations to the removal of phosphate in return. Additionally, Koilraj and Kannan (2010) demonstrated that in the coexisting system of phosphate and Zn^{2+}, chemical precipitates of phosphate and Zn^{2+} would happen which caused the co-removal of phosphate and Zn^{2+}. Their results provide a reason for the similar removal efficiencies of phosphate at the solution with and without heavy metal cations (Fig. 4) and the constant removal rates of Zn^{2+} (i.e., ~20%) under the coexistence of phosphate even at very low solution pH (Table S6).

4. Conclusions

In conclusion, Mg/Al-CLDH was effective in pH neutralization and various contaminants removal for acidic wastewater. The possible mechanism of heavy metal cation removal occurred mainly along with the rehydration process of Mg/Al-CLDH (i.e., rising solution pH) and via the formation of hydrogen bonds with the reconstructed LDH. The coexistence of heavy metal cations and anionic contaminants like Cr (VI) and phosphate would impact the removal behavior for both heavy metal cations and anions. For the influences of heavy metal cations toward the removal of Cr(VI) and phosphate: heavy metal cations weakened the removal of Cr(VI) by competing for the adsorption sites on the R-LDH, while they only showed slight impact to the removal of phosphate. For the influences of Cr(VI) and phosphate toward the removal of heavy metal cations: a low concentration of Cr(VI) greatly improved the removal of heavy metal cations by providing extra adsorption sites, and by possibly promoting the formation of $M(OH)^+$. A high concentration of Cr(VI) might largely occupy the adsorption sites on the reconstructed LDH, thus inhibited the removal of heavy metal cations. Phosphate significantly inhibited the removal of heavy metal cations, which might be ascribed to the strong buffering ability of phosphate that maintained the strong acidic nature of the coexisting solution of heavy metal cations and phosphate, and the ionization of $H_2PO_4^-$ badly inhibited the formation of $M(OH)^+$. This work provides new insight into the use of CLDH in acidic wastewater treatment for acidity neutralization, heavy metal cations removal, and the co-removal of heavy metal cations and anionic contaminants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2017.12.002.

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