



Research paper

Efficient removal of copper and lead by Mg/Al layered double hydroxides intercalated with organic acid anions: Adsorption kinetics, isotherms, and thermodynamics



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ABSTRACT

Mg/Al layered double hydroxides (LDH) directly intercalated with organic anions (citrate and malate) were synthesized through a co-precipitation method at low supersaturation, yielding Citrate-LDH and Malate-LDH, respectively. Three obtained LDH samples were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, zeta potential, and scanning electron microscopy. The results indicated that the organic anions were intercalated into the interlayer region of LDH as a horizontal orientation. The adsorption capacity of the LDH samples toward Cu(II) and Pb(II) ions was strongly affected by the solution's pH, with the highest adsorption capacity reaching at pH 5.0. As revealed in the kinetic study, equilibrium was rapidly established with adsorption half-lives at 30 °C in the range of 7.38–11.4 min for Cu(II) adsorption and 1.59–3.87 min for Pb(II) adsorption. The maximum Langmuir adsorption capacity of Pb(II) and Cu(II) cations at 30 °C exhibited the following order: Citrate-LDH (166 mg/g and 137 mg/g) > Malate-LDH (141 mg/g and 118 mg/g) > pristine LDH (84.7 mg/g and 59.9 mg/g), respectively. Thermodynamic studies demonstrated that the adsorption process was spontaneous ($-\Delta G^\circ$), endothermic ($+\Delta H^\circ$), and increasingly random ($+\Delta S^\circ$). The results demonstrated that the intercalation of citrate and malate anions into LDH successfully resulted in improving the adsorption capacity and rate of potentially toxic cations.

1. Introduction

Layered double hydroxides (LDH) are commonly known as synthetic anionic clays or hydrotalcite-like materials that are biocompatible systems. LDH is a class of layered materials comprising (1) positively charged brucite-like layers, and (2) non-framework charge compensating anions in interlayer galleries (also known as interlayer regions). The interlayer galleries of LDH typically contain charge-balancing anions (i.e., OH^- , Cl^- , SO_4^{2-} , NO_3^- , and CO_3^{2-}) and water. The general form of LDH can be given as $[\text{M}_1^{2+}_x\text{M}_2^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} represents for divalent metal cations, M^{3+} for trivalent metal cations, and A^{n-} for the interlayer anions of valence n (relatively easily replaced). The molar ratio x is defined as $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, normally ranges from 0.20 to 0.33. Essentially, the divalent cations often comprise Mg, Mn, Fe, Co, Ni, Cu, and Zn with ionic radii ranging from 0.65 to 0.80 Å; other divalent cations with higher ionic radii (such as Ca, Cd,

Sc, and La) may be incompatible with the formation of true brucite-like layers. Meanwhile, the trivalent cations frequently include Al, Mn, Fe, Co, Ni, Cr, and Ga (with ionic radii stemming from 0.62 to 0.69 Å, exception for Al: 0.50 Å) (De Roy et al., 2001; He et al., 2006).

Notably, the unique structural features of LDH will be strongly dependent on their synthesis methods. Various techniques of LDH synthesis have been reported in the literature, such as coprecipitation, ion exchange, reconstruction, and hydrothermal method. Among them, the coprecipitation can be considered the most common synthesis method literature (He et al., 2006; Goh et al., 2008). Generally, the precipitation method at low supersaturation is based on the dropwise addition of a solution (i.e., divalent and trivalent metal salts mixed with adequate proportions) into a reactor containing water. Another solution (i.e., NaOH solution) is simultaneously added into the reactor to maintain the solution pH at a targeted value. As a coprecipitation result of the two metallic salts, a gel was formed. In addition to the

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forementioned coprecipitation method, a subsequent hydrothermal treatment (also known as hydrothermal carbonation of LDH in a temperature-controlled autoclave) can further enhance the crystallinity of amorphous or poorly crystallized materials (De Roy et al., 2001; He et al., 2006; Goh et al., 2008). In addition to generic LDHs, Newman and Jones (1998) pointed out four general approaches to the preparation of organic anion-containing layered double hydroxides (organo-LDH) as follows: anion-exchange of a precursor LDH; direct synthesis by coprecipitation; rehydration of a calcined LDH precursor, and thermal reaction.

Both LDH and organo-LDH have garnered increasing attention due to their versatility, easily manipulated properties, preparation variables, and cost efficiency. They are commonly applied in catalysis, ion-exchange and adsorption, miscellaneous, pharmaceuticals, photochemistry, and electrochemistry (Newman and Jones, 1998; Li and Duan, 2006). In water decontamination, LDH and organo-LDH can potentially be used as promising adsorbents to remove toxic metal cations and anions from aqueous media. Previous studies demonstrated that LDH intercalated with amino acids (Tran et al., 2018a), ethylenediaminetetraacetic acid (Pérez et al., 2006), glutamate (Yanning et al., 2017), and diethylenetriaminepentaacetate and meso-2,3-dimercaptosuccinate (Pavlovic et al., 2009), possessed a higher affinity to potentially toxic metal cations (i.e., Cu^{2+} , Cd^{2+} , Ni^{2+} , and Pb^{2+}) than the pristine LDH adsorbents. The presence of potentially toxic metals in water and wastewater is an enormous health public concern because of their toxic and carcinogenic nature. Therefore, the World Health Organization sets the limit of concentration in drinking water to 0.003 mg/L for Cd, 1.0 mg/L for Cu, 0.0015 mg/L for Pb, 0.001 mg/L for Hg, 0.02 mg/L for Ni, and 5.0 mg/L for Zn (Siegel, 2002).

Citric and malic acids—a dicarboxylic acid—exists abundantly in nature. Similar ethylenediaminetetraacetic acid, they are also considered as an excellent chelating agent in binding toxic metal cations. Therefore, the citrate and malate anions-intercalated LDHs are expected as a potential adsorbent for removing potentially toxic metal ions in commercial-scale applications (Kameda et al., 2008a). In this study, we prepared organic acid anions (i.e., citrate and malate) intercalated LDHs through a co-precipitation method at low supersaturation. The LDH samples were characterized by various techniques, i.e., X-ray diffraction, Fourier transform infrared spectroscopy, zeta potential, and scanning electron microscopy, and applied to remove two potentially toxic metals (lead and copper). The effects of various operation conditions including solution pH, initial metal concentration, and temperature were examined in batch experiments. The investigation of kinetic, isotherm, and thermodynamic adsorption was thoroughly discussed herein.

2. Experimental section

2.1. Materials

All chemicals were of analytical reagents grade and used without further purification. Magnesium nitrate hexahydrate and aluminium nitrate nonahydrate were purchased from Alfa Aesar. Sodium hydroxide puriss and sodium carbonate obtained from Sigma-Aldrich and Baker, respectively. Organic acids (i.e., citric and malic acids) and metal cations (copper and lead) were purchased from Merck. All solutions in this study were prepared with deionized distilled high purity water obtained from a Milli-Q water (Millipore) system.

2.2. Preparation of CO_3 -LDH and organic acid anions-intercalated LDH

A layered magnesium/aluminium double hydroxide containing intercalated carbonate (pristine Mg/Al-LDH) was prepared following a standard aqueous precipitation and thermal crystallization method published elsewhere (Reichle, 1985; Whilton et al., 1997). Specifically, a solution containing 0.12 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.04 mol Al

$(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 60 mL deionized water was added dropwise under mild stirring into another solution comprising 0.336 mol NaOH (pH = 12) and 0.022 mol Na_2CO_3 in 40 mL deionized water. The resultant gel was aged with stirring at 45 °C for 24 h. Subsequently, approximately 150 mL deionized distilled water was added and vigorously stirred for 1 h. The mixture was transferred into a 200 mL Teflon-lined autoclave. After a 24 h hydrothermal process at 190 °C, the obtained precipitate (white powder) was collected by filtration, washed repeatedly with deionized water until the pH of the filtrate reaching 7.0, dried at 65 °C for 48 h, and stored in airtight brown bottles.

The LDH intercalated with citrate and malate anions were directly synthesized by a homogeneous coprecipitation method (Kameda et al., 2008b; Tran et al., 2018a). Typically, the Mg–Al mixture comprised of 93.75 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 31.25 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 250 mL of deionized water to form a clear solution. The solutions of organic acids were obtained by dissolving 20.83 mmol of citrate or 31.25 mmol of malate in 250 mL deionized water. Subsequently, the Mg–Al solution was added dropwise, under gentle agitation, to the solutions of organic acids at a rate of 10 mL/min at 30 °C. The pH of reaction mixture was adjusted and maintained to 10 ± 0.2 by adding 0.5 M NaOH solution. To avoid the effects of dissolved CO_2 , nitrogen gas was bubbled into the solutions during the procedure. After completion of the dropwise addition, the resulting suspensions were allowed to settle at ambient temperature for 1 h (solution pH maintained at 10 ± 0.2). The precipitate (white powder) was subsequently isolated by centrifugation, washed repeatedly with deionized water, and dried in a vacuum oven at 65 °C for 48 h, and stored in tightly closed brown bottles. For convenience, the Mg/Al layer double hydroxides intercalated with citrate and malate anions were referred as Citrate-LDH and Malate-LDH, respectively.

Notably, previous studies demonstrated that the hydrothermal method was usually used when organic guest anions (i.e., deoxycholic acid) with low affinity for LDH. This means that the organic guest anions are difficult to be intercalated into the interlayers of LDH (Ogawa and Asai, 2000; Goh et al., 2008). According to the findings of other scholars, layered double hydroxides can be directly intercalated with organic anions (i.e., citrate and malate) through the coprecipitation method (Kameda et al., 2008a; Perera et al., 2015).

2.3. Characterization of pristine LDH and intercalated LDH

X-ray diffraction (XRD) data were collected on a PANalytical PW3040/60 X' Pert Pro, with Cu $\text{K}\alpha$ radiation (45 kV, 40 mA) and wavelength $\lambda = 1.54 \text{ \AA}$. The scan angle covered $5^\circ < 2\theta < 70^\circ$ at a scan speed of $3^\circ/\text{min}$. Fourier transform infrared (FT-IR) spectra were recorded with a PerkinElmer 1600 FT-IR spectrophotometer. The spectra were scanned from 4000 cm^{-1} to 650 cm^{-1} . Morphological features were studied using a scanning electron microscope (SEM, S-3000N, Hitachi). The textural properties were measured by collecting nitrogen adsorption/desorption isotherms (Micromeritics ASAP 2020 sorptometer) at 77 K. A zeta potential analyser (Colloidal Dynamics; ZED-3600) measured the zeta potential of various pH values of the LDH samples. Before analysing their characteristics, the LDH samples were dried in a vacuum oven using N_2 gas at 115 °C for 24 h.

2.4. Adsorption study

All copper and lead solutions were diluted from stock solutions (1000 mg/L). The stock solutions were prepared by dissolving Cu $(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ or Pb $(\text{NO}_3)_2$ in deionized distilled water.

The adsorption process of target toxic metals was conducted in batch experiments. Approximately 0.1 g of adsorbent (i.e., LDH, Citrate-LDH, or Malate-LDH) was added to 100 mL of aqueous adsorbate solution (i.e., copper or lead) in 250-mL Erlenmeyer flask. The flask was covered with a parafilm and was shaken at 150 rpm in a water batch isothermal shaker (DKW-20; Deng Yng Co.) until desirable time

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