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Factors influencing the chloride removal of aqueous solution by calcined layered double hydroxides

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ABSTRACT

Chloride removal of aqueous solution by calcined layered double hydroxides (CLDH) was investigated in batch model. The influences of calcination temperature, Mg/Al molar ratio of CLDH, initial chloride concentration, and the presence of other anions on chloride removal from aqueous solution have been discussed in detail. It was found that the LDHs with an Mg/Al ratio of 4 calcined at 500°C had the highest removal capacity. The chloride removal capacity of CLDH decreasing with a rise in the temperature indicated that the process is exothermic in nature. And the data of sorption isotherms fitted well into the linearly transformed Langmuir equation. The negative values of ΔG^0 and ΔH^0 calculated using Langmuir constants, confirm the spontaneous and exothermic nature of chloride removal process. In addition, regeneration of the spent CLDH adsorbent was also studied in order to assess the potential for recycling the material. The explanations of chloride removal and regeneration phenomena have been supported by X-ray diffraction (XRD) and thermo-gravimetric/differential thermal analyzer (TG-DTA).

Keywords: Layered double hydroxides; Calcined; Chloride removal; Sorption isotherms

1. Introduction

Wastewater containing chloride ions is often discharged from landfills [1,2], tanning industries, and pickling industries [3,4]. The high salt content in the wastewater can give rise to corrosion of waste pipes [1] and pose problems in treatment systems particularly in biological units. Chloride induced is a well-known problem, especially where de-icing salts, chloride-containing admixtures or chloride contaminated aggregate are incorporated into the concrete [5].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds are a class of synthetic anionic layered clays as containing brucite-like layers and positively-charged sheets. The general formula is $[\mathrm{M^{II}}_{1-x}\mathrm{M^{III}}_x(\mathrm{OH})_2]^{x+}(\mathrm{A}^{n-})_{x/n}\cdot y\mathrm{H_2O}$, where M^{2+} and M^{3+} represent divalent and trivalent cations in the octahedral sites within the hydroxyl layers, x is equal to the ratio of $\mathrm{M}^{3+}/(\mathrm{M}^{2+}+\mathrm{M}^{3+})$ with a value varying in the range of 0.17–0.50, and A is the exchange interlayer anion [6]. LDHs calcined within a certain temperature range (CLDH) have been shown to reconstruct their original layered structure in the presence of aqueous solution of appropriate anions. Therefore, CLDH has been studied as potential adsorbents for removing harmful anionic from aqueous systems [7–14]. In our previous work, it was also indicated that the CLDH can effectively removal halide ions, phosphate, and perchlorate from water [15,16].

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Although the kinetic studies on chloride removal by CLDH have been reported in our group [15,17], to understand the simulation of actual industrial applications, more work was necessary. The primary objectives of the reported study were to evaluate the removal of chloride in batch systems using CLDH, taking into account the effects of calcination temperature, Mg/Al molar ratio of CLDH, initial chloride concentration, and presence of other anions on chloride removal from aqueous solution. The thermodynamic parameters were calculated from sorption isotherms. In addition, regeneration of the spent CLDH adsorbent was studied in order to assess the potential for recycling the material. The explanations of chloride removal and regeneration phenomena have been supported by X-ray diffraction (XRD) and thermogravimetric-differential thermal analyzer (TG-DTA). The results reported here show that these factors affect the chloride removal and are significant towards a better understanding of the potential application of CLDH for chloride removal of contaminated water.

2. Materials and methods

2.1. Materials

$Mg(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, NaOH, Na_2CO_3, and NaCl were analytical reagent (A.R.) grade, used as received. All the water used was deionized. The chloride ion aqueous solution used in this study was pure. The standard chloride solutions used in the experiments were prepared from anhydrous NaCl. MgAl-CO_3 LDHs was obtained by using a conventional co-precipitation method [15–17]. The method involves very rapid mixing to complete the nucleation process, followed by a separate aging process. CLDH was obtained by calcining LDHs in a muffle furnace at designated temperature (200–800°C) for 3 h.

2.2. Characterization

XRD pattern of the samples, including MgAl-CO_3 LDHs, CLDH and CLDH after chloride removal, were obtained using a Shimadzu XRD-6000 diffractmeter with Cu Kα radiation (40 kV and 30 mA) at a scanning rate of 5°min^{-1}. Simultaneous TG-DTA was carried out in air on a PCT-1A thermal analysis system produced locally. Samples of MgAl-CO_3 LDHs precursor and CLDH after chloride removal (9.0–10.0 mg) were heated at a rate 10°C/min up to 600°C. Elemental analysis was performed by inductively coupled plasma (ICP) emission spectroscopy with a Shimadzu ICPS-7500 ICP instrument using solutions prepared by dissolving the samples in dilute HNO_3.

2.3. Sorption experiments

CLDH samples (4.0 g) were dispersed in 2 L of chloride solutions with a concentration of 100 mgCl^-/L and stirred for 6 h, under N_2 atmosphere. 5 mL aliquots were extracted at selected time intervals, separated by filtration, and diluted to 50 mL. Chloride ions concentration was measured in the solution using a selective electrode for chloride ions, and the solid remaining at the end of the experiment was characterized by XRD and TG-DTA. The chloride concentration and chloride removal capacity of CLDH was calculated, respectively.

Sorption isotherm studies were conducted in a series of 250 mL flask by mixing 100 mL of chloride solution (10–1,000 mg/L) with 0.20 g CLDH. The mixture was shaked at designated temperature for 24 h under N_2 atmosphere. The pH of the solution was not adjusted. After shaking 24 h to allow the uptake of chloride until equilibrium was reached, the mixture was then filtered. Chloride ions concentration was measured in the solution using a selective electrode for chloride ions, and the solid remaining at the end of the experiment was characterized by XRD and TG-DTA. Removal capacity by the CLDH was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}, \tag{1}$$

where q_e is the removal capacity at equilibrium in mg/g, C_0 and C_e are initial and equilibrium concentrations of chloride in mg/L, V is the volume of solution in liters, and m is the mass of CLDH in grams.

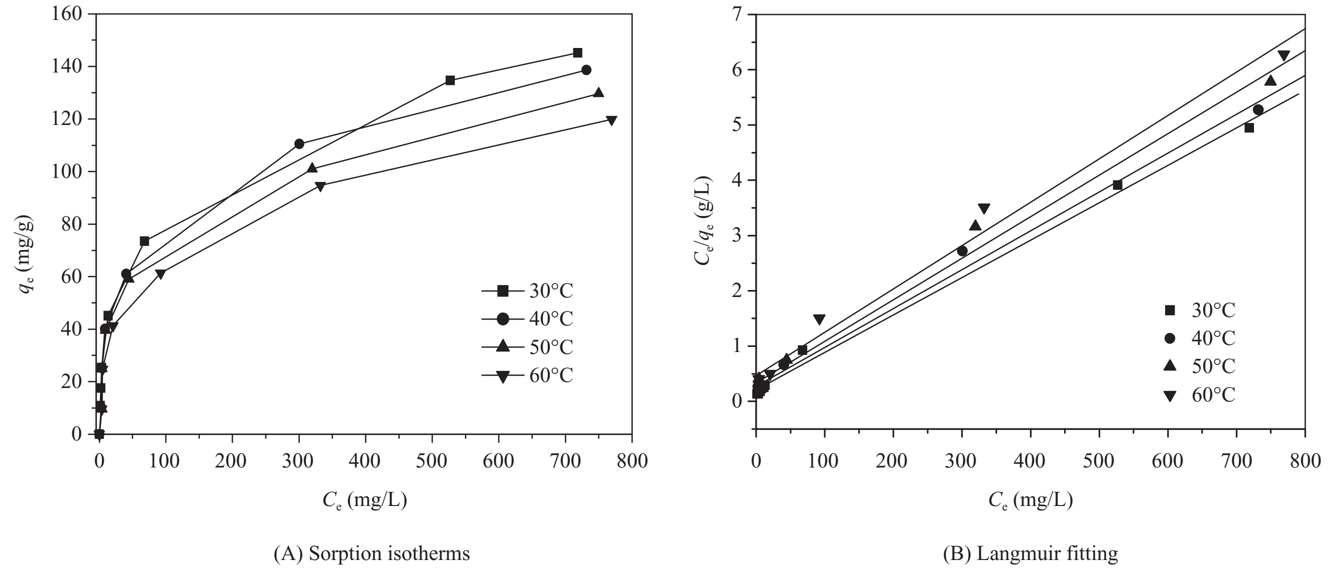
2.4. Regeneration and recycling studies

The regeneration studies were carried out using Na_2CO_3 aqueous solution (0.1 M). The mixture was stirred for 6 h, and the resulting solid was then filtered, washed thoroughly with deionized water, and calcined in a muffle furnace at 500°C for 3 h.

3. Results and discussion

3.1. Sorption isotherms

Fig. 1A is the sorption isotherms of chloride removal by CLDH at different temperature, which indicates that the chloride removal capacity increases upon increasing equilibrium concentration of chloride and decreasing temperature. The observation shows that the interaction between adsorbate and adsorbent is exothermic in nature, even though the change in the temperature does not influence the equilibrium time and the removal curve is smooth and continuous. The



(A) Sorption isotherms

(B) Langmuir fitting

Fig. 1. The sorption isotherms of chloride removal by CLDH.

temperature dependence of chloride removal process is associated with several thermodynamic parameters.

The data were further analyzed by the linearly transformed Langmuir, and it is shown in Fig. 1B and Table 1

$$C_e/q_e = 1/K_L q_m + C_e/q_m, \quad (2)$$

where K_L is the Langmuir constant related to the loading and energy of chloride removal; q_m the maximum chloride removal capacity; q_e the chloride removal loading at equilibrium (mg/g), and C_e is the equilibrium concentration of chloride in the solution (mg/L), respectively.

Thermodynamic parameters such as Gibbs free energy (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) for the process were calculated using the equations [16]:

$$\Delta G^0 = -RT \ln K_L, \quad (3)$$

$$\ln K_L = \Delta S^0/R - \Delta H^0/(RT), \quad (4)$$

where R is universal gas constant, T is temperature (K), and K_L is Langmuir constant. The values of ΔG^0, ΔH^0 and ΔS^0 are also listed in Table 1. The negative ΔG^0 value indicates the spontaneity of the chloride removal process. ΔH^0 and ΔS^0 were calculated from a Van't Hoff plot (not shown here, correlation coefficient $R^2 = 0.991$) using the slope and intercept by regression method, respectively. The negative value of ΔH^0 confirms the exothermic nature of chlorination by CLDH which has been predicted earlier from Fig. 1A. The positive value of ΔS^0 suggests the increased randomness at the solid/solution interface for the chloride removal process.

3.2. *Effect of calcination temperature of MgAl-CO$_3$ LDHs*

The chloride removal by the as-synthesized LDHs and LDHs calcined at various temperatures was investigated. Relationship between the removal capacity by LDHs calcined at different temperatures and the time are shown in Fig. 2. It can be seen that the removal capacity by LDHs calcined at 500°C is the highest, reaching 50 mg/g. The removal capacity

Table 1
Langmuir constants and thermodynamic parameters associated with chloride removal by CLDH

Temp (°C)	q_m (mg/g)	K_L (L/mol)	Ln K_L	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
30	149.5	1151.0	7.05	−17.77	−17.52	0.89
40	142.2	916.1	6.82	−17.76		
50	133.2	795.4	6.68	−17.95		
60	127.4	599.3	6.40	−17.72		

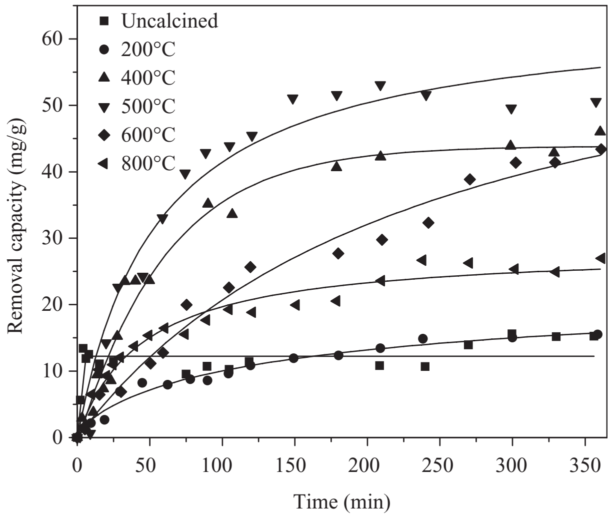


Fig. 2. Effect of calcinations temperature of CLDH on the chloride removal.

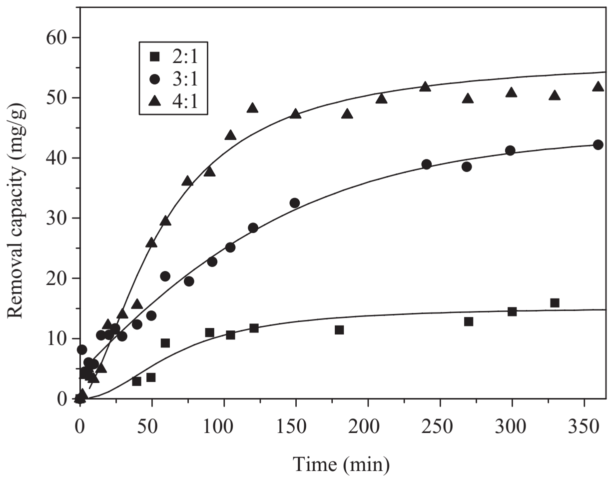


Fig. 3. Effect of Mg/Al molar ratio of CLDH on the chloride removal.

by LDH as precursor (13.9 mg/g) is the lowest of all. It increases with calcination temperature between 200 and 500°C, but decreases from 500 to 800°C. Because LDHs transforms to aluminum and magnesium oxides by lose of interlayer anions, the interlayer carbonate of LDHs is decomposed completely when calcined at 500°C [17]. When the calcination temperature is above 500°C, CLDH is transformed into a spinel that does not exhibit the property of reconstruction, which results in the observed decrease in the removal capacity.

3.3. Effect of Mg/Al molar ratio of LDHs layers

The effect of varying Mg/Al molar ratio of LDHs on the chloride removal was investigated. Fig. 3 shows that the retention of chloride by the CLDH with Mg/Al molar ratio of 4 is the best of all, for which the removal capacity reached 50 mg/g. The removal capacity by CLDH with Mg/Al ratios of 4, is higher than that of 2 and 3, due to the gallery height (means ''spacing of layer and layer'') of LDHs with an Mg/Al ratio of 4 higher than with that of 2 and 3.

3.4. Effect of initial chloride concentration

The effect of the initial chloride concentration on the process of adsorption for the CLDH (2.0 g/L) was studied and shown in Fig. 4. It can be seen that the percentage of removal increases with decreasing the initial of chloride concentration. When the initial concentration of chloride is 70 mg/L, the percentage of removal is higher than 99.9%, however, the removal capacity of CLDH is decreased to 34.97 mg/g. It is obvious in Fig. 4 that removal capacity of CLDH increases with the decrease in the initial chloride concentration from 100 to 2,000 mg/L, reaching 179.72 mg/g from 49.60 mg/g.

The distribution coefficient K_D (L/g), describing the binding ability of adsorbent surface for an element, is calculated as the following equation:

$$K_D = C_s/C_w, \tag{5}$$

where C_s is the concentration of chloride on solids (mg/g) and C_w is the concentration of chloride in water (mg/L).

It can be seen from Fig. 4 that the distribution coefficient (K_D) increases with increasing initial chloride concentration in the range of 20–70 mg/L and

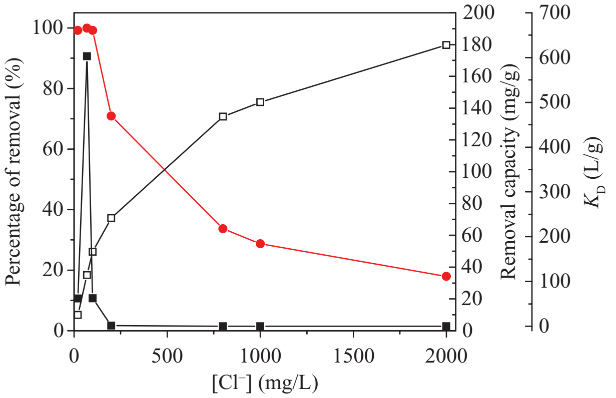


Fig. 4. Effect of initial chloride concentration on the chloride removal. (□) removal capacity vs. initial chloride concentration; (●) percentage of removal vs. initial chloride concentration; (■) distribution coeffient K_D vs. initial chloride concentration.

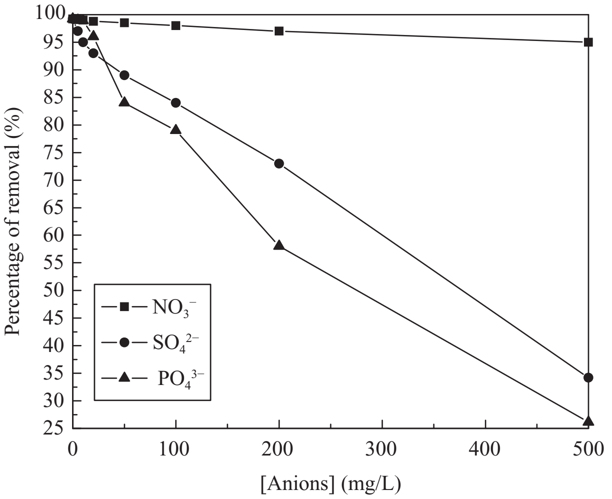


Fig. 5. Effect of other anions on the chloride removal.

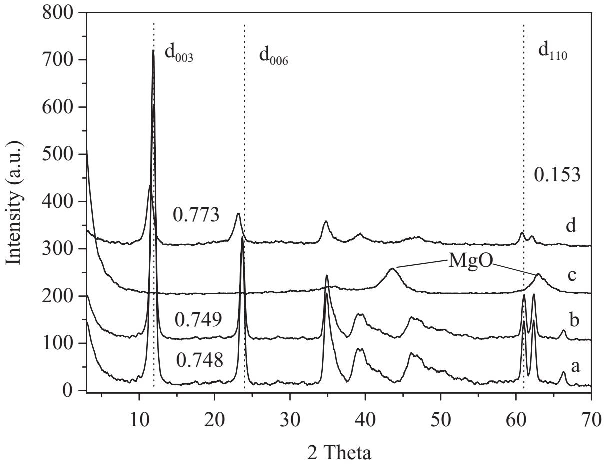


Fig. 6. Powder XRD patterns for (a) MgAl-CO_3 LDHs, (b) LDHs after chloride removal, (c) CLDH, (d) CLDH after chloride removal.

decreases with increasing initial chloride concentration in the range of 70–2,000 mg/L.

3.5. Effect of other anions

A variety of other anions is generally present in chloride-containing wastewater, and may compete with chloride for adsorption on the LDHs. The effects of added SO_4^{2-}, NO_3^-, and PO_4^{3-} were studied in this work and the results are shown in Fig. 5. It can be found that the co-existing anions in solution lead to the decrease of removal capacity of CLDH for Cl^- in the order of $PO_4^{3-} > SO_4^{2-} \gg NO_3^-$. The effect of these anions towards chloride removal may be due to their affinity towards CLDH. CLDH have greater affinities for anions with higher charge density, i.e., multicharge anions get adsorbed more easily than that of monovalent anions.

3.6. Recycling and regeneration of CLDH

In order to recycle the adsorbent, it is necessary to have a high recovery ratio of CLDH after treatment with chloride, where the recovery ratio means the ratio of quantity of LDHs after removal to that before removal. The values of recovery ratio after removal of chloride are nearly 95%.

Successive sorption measurements (Table 2) show that the regenerated CLDH has almost the same capability of removal of chloride ions as fresh CLDH. It can be concluded that the removal of chloride is a reversible process, thereby facilitating the recycling of the material for further use.

3.7. Mechanism confirmed

The XRD pattern of the MgAl-CO_3 LDHs (Fig. 6a) shows sharp and symmetric peaks at lower 2θ values, which are characteristic of hydrotalcite-like compounds, and the material consists of one phase only [6]. However, the LDHs after uptake of chloride gives a basal spacing of 0.749 nm (Fig. 6b), which is almost the same as that of LDHs precursor. Because the affinity of chloride ion towards LDHs is much lower than that of LDHs towards carbonate, the ion-exchange of chloride ion for carbonate in LDHs interlayer is difficult. As a result, the chloride removal by MgAl-CO_3 LDHs mainly occurs on the surface of LDHs. After the LDHs calcined at 500°C, the layered hydrotalcite-like structure is absent

Table 2
Relationship between the percentage of removal, removal capacity and number of times recycled (V = 50 mL, T = 30 °C, $[Cl^-]_0 = 100$ mg/L, $w_{adsorbent} = 0.1$ g)

Cycle number	1	2	3	4	5
Percentage of removal (%)	98.99	99.12	98.94	97.64	97.28
Removal capacity (mg/g)	49.49	49.56	49.47	48.82	48.64

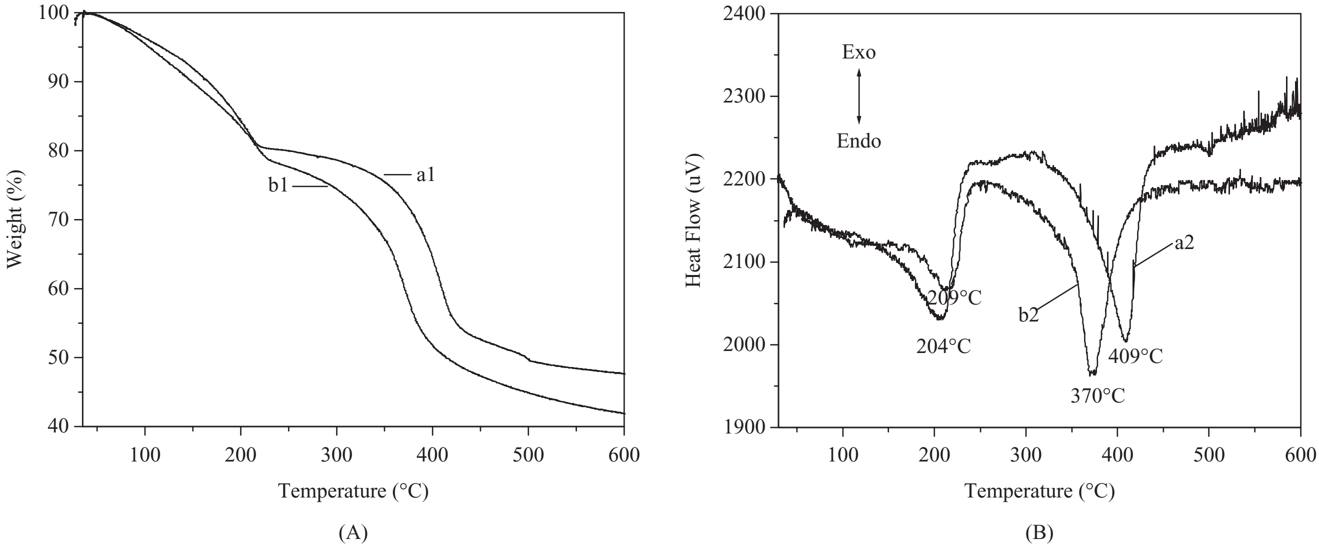


Fig. 7. TG and DTA profiles for (a) MgAl-CO_3 LDHs and (b) CLDH after chloride removal.

(Fig. 6c), leading to the formation of magnesium aluminum oxide. But after chloride adsorption, reconstruction of the structure (Fig. 6d) has been observed to take place, the re-constructed LDHs exhibits a d_{003} of 0.773 nm (11.43°), larger than 0.748 nm (11.82°) of MgAl-CO_3 LDH precursor. This indicates that the formation of MgAl-Cl LDHs. Chemical analysis indicates that the CLDH after chloride removal has an Mg/Al molar ratio of 3.89:1, the same as that of the CLDH itself (Mg/Al molar ratio of 3.92:1).

The TG and DTA curves of the MgAl-CO_3 LDHs precursor and CLDH after chloride removal are shown in Figs. 7A and 7B, respectively. The thermal decomposition of the CLDH after chloride removal is characterized by two weight loss steps (See Fig. 7b1): the first one from room temperature to 238°C can be attributed to the removal of surface adsorbed water, carbonate and interlayer water molecules, with one corresponding endothermic peak (209°C) in the DTA curve (Fig. 7b2); the second step (238–450°C), involving a gradual weight loss, is the result of the deintercalation of Cl^- and dehydroxylation of the brucite-like layers, with a corresponding endothermic peak (370°C) in the DTA curve (Fig. 7b2). In the case of MgAl-CO_3 LDHs, the two steps weight loss steps (with corresponding endothermic peaks at 204 and 409°C) (Figs. 7a1 and a2) are attributed to removal of interlayer water and carbonate anion.

Based on the above results, the mechanism of chloride removal by CLDH is confirmed to be rehydrated with incorporation of chloride ion, to reform a layered structure.

4. Conclusions

The removal capacity of CLDH increases with increasing the initial chloride concentration, but decreases with increasing temperature. The distribution coefficient is the highest when initial chloride concentration is 70 mg/L. The co-existing anions in chloride aqueous solution influences the capacity of CLDH for Cl^- in the order of $PO_4^{3-} > SO_4^{2-} > NO_3^-$. The surface sites become less active with increased temperature, and as a result the fraction of chloride removal decreases. The negative ΔG^0 value indicates the spontaneity of the chloride removal process. The negative value of ΔH^0 confirms the exothermic nature of chloride removal. The XRD patterns and TG-DTA profiles confirmed that the mechanism of chloride removal is the reconstruction of CLDH to LDH with chloride as interlayer anions. The CLDH can be used as an effective material to remove to chloride from aqueous solution, and the process is reversible.

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