

# Synthesis and sulfate ion-exchange properties of a hydrotalcite-like compound intercalated by chloride ions

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## Abstract

To reduce the generation of hydrogen sulfide gas from sulfate ions, we synthesized a layered double hydroxide hydrotalcite-like compound intercalated with chloride ions in the interlayer (HT-Cl) using a coprecipitation reaction. The resultant HT-Cl material had a Mg/Al molar ratio of approximately 2, and the molar fraction of the chloride ions on the intercalated anion layer of the HT was 0.90. A higher molar fraction of chloride ions can be inserted into the interlayers of the HT by increasing the initial concentration ratio of chloride ions to aluminum ions  $[Cl^-]_0/[Al^{3+}]_0$  in the solution. Approximately 98% of the sulfate ions in the solution were removed within 10 min after adding 1.12 times the stoichiometric quantity of synthesized HT-Cl, which contained a Mg/Al molar ratio of 2 equal to a solution containing a 12 mM calcium sulfate solution.

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## 1. Introduction

A serious environmental issue has been raised by the detection of high concentrations of harmful hydrogen sulfide gas in many anaerobic subsurface environments, such as landfill sites. Current measures, such as capture-fixed methods or diffusion, are being applied to the emission of hydrogen sulfide gas, which is principally due to the reduction of sulfates by sulfate-reducing bacteria, linked to the degradation of naturally occurring and contaminant forms of organic matter under anaerobic conditions [1–3]. In these cases, one of the methods for controlling the emission of H<sub>2</sub>S gas is to remove the sulfate ions (SO<sub>4</sub><sup>2-</sup>), *i.e.*, the source of the sulfur, thereby moderating the activity of sulfate-reducing bacteria.

Traditionally, the use of clay material as an anion exchanger is a method used for removing SO<sub>4</sub><sup>2-</sup> to lower the emission of harmful gases into the environment. Hydrotalcite-like compounds (HTs) are layered double hydroxides with anion-exchange properties [4,5]. The chemical composition of a

HT is Mg<sub>1-x</sub><sup>2+</sup>Al<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, where A<sup>n-</sup> is an *n* valent anion, such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, or Cl<sup>-</sup>, and 0.20 ≤ *x* ≤ 0.33. The crystal structure consists of positively charged brucite-like octahedral hydroxide layers, which are charge neutralized by the interlayer anion. Water molecules occupy the remaining interlayer space inside the crystal lattice. Since CO<sub>3</sub><sup>2-</sup> has an exceptionally high affinity for HTs, CO<sub>3</sub><sup>2-</sup> intercalated in the interlayer (HT-CO<sub>3</sub>) is a preferred solution, which can be synthesized using a coprecipitation method. An aqueous solution containing Mg<sup>2+</sup> and Al<sup>3+</sup> ions is continuously added to the appropriate aqueous solution of anions at a slow flow rate maintaining at pH from 8 to 10 by the drop-wise addition of a base such as NaOH and/or Na<sub>2</sub>CO<sub>3</sub>. This method can yield HTs intercalated with anions such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, and Cl<sup>-</sup> in interlayers [6–9]. It has been reported that Cl<sup>-</sup>-intercalated hydrotalcite (HT-Cl) [10,11] is an excellent phosphate ion exchanger [12–14].

The selectivity for the HT increases with the increasing electric charge of the anion and decreasing anion size, for example, CO<sub>3</sub><sup>2-</sup> > SO<sub>4</sub><sup>2-</sup> > OH<sup>-</sup> > F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> [7,15]. The anion, which has the highest electric density, exhibits the highest electrostatic force toward the host layer. When a higher amount of Cl<sup>-</sup> is intercalated inside the HT layer, a smaller concentration of CO<sub>3</sub><sup>2-</sup> and/or OH<sup>-</sup> is present in the intercalated layer; therefore, the SO<sub>4</sub><sup>2-</sup> in the solution can be removed more

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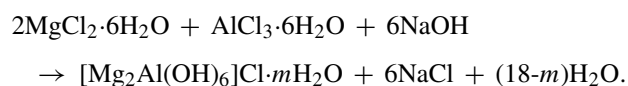
effectively. The charge density in the interlayer is proportional to the number of  $\text{Al}^{3+}$  ions, and the number of intercalated anions is determined by the charge density. The selectivity for the HT increases with anions containing a higher electric field density due to a higher electrostatic field interaction between the HT and the anion.  $\text{SO}_4^{2-}$  can be intercalated in the HT more rapidly than other anions, decreasing the Mg/Al molar ratio in the host layer. Consequently, HT-Cl, in which the Mg/Al molar ratio is 2, is highly suitable for removing the  $\text{SO}_4^{2-}$  in the solution.

In this study, we prepared a HT-Cl material containing a Mg/Al molar ratio of 2, and conducted experiments examining the possible variables to reduce  $\text{SO}_4^{2-}$  by varying the concentrations of  $\text{MgCl}_2$  and  $\text{AlCl}_3$  in the solution, the aging time, and the dripping method for the solution. We report the conditions for synthesizing the optimal ratio of  $\text{Cl}^-$  intercalated within the HT, and describe the  $\text{SO}_4^{2-}$  exchange for the synthesized HT-Cl material.

## 2. Materials and methods

### 2.1. Synthesis of $\text{Cl}^-$ -intercalated hydrotalcite

The HT-Cl was prepared using a standard coprecipitation method (*i.e.*, mixing  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  solutions, which had a  $[\text{Mg}^{2+}]_0/[\text{Al}^{3+}]_0$  molar ratio of 2 and total  $[\text{Mg}^{2+}]_0$  and  $[\text{Al}^{3+}]_0$  concentrations of 1 M) in water or NaCl solution in a five-necked, round-bottomed flask using a peristaltic pump at a rate of 5 ml/min. The resulting solution was kept at pH 10 by adding 2 M sodium hydroxide solution using a peristaltic pump through another port in the flask. Two glass bars were placed between the injection ports for the added solutions and bulk solution in order to add solutions that were moving along the glass bars to the bulk solution continuously. The solution was stirred at 600 rpm and 25 °C, continuously venting the nitrogen gas in order to prevent carbon dioxide gas from being dissolved. A pH of 10 was kept constant to maintain the following stoichiometric equation:

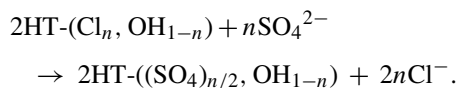


The formed precipitate was stirred between 1 and 24 h at 300 rpm and 70 °C, and then cooled at ambient temperature for 2 h. The HT-Cl material was isolated by centrifuging the resulting suspension, washing it four times with deionized water, and drying it at 105 °C for 24 h. The precipitates were analyzed by X-ray diffraction (XRD) using a Rigaku Denki RINT-2200VHF. The precipitates were dissolved with nitric acid and the chloride concentration was determined by ion chromatography using Dionex QIC and a Dionex model AS4A column (eluent: 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate, flow rate: 1.5 ml/min, detection limit: 0.06 mg/l). The Mg and Al concentrations were quantified by ICP-AES using a Seiko Instruments SPS7800. The hydroxide concentration in the HT-Cl material was estimated from a charge balance assuming that the excess charge with the  $\text{Al}^{3+}$  ion in the host layer was compensated by the  $\text{Cl}^-$  and  $\text{OH}^-$ .

### 2.2. $\text{SO}_4^{2-}$ removal by HT-Cl

A solution containing 1.2–12 mM  $\text{CaSO}_4$  with a volume of 30 ml and a prescribed amount of HT-Cl (chemical composition:  $[\text{Mg}_{1.98}\text{Al}(\text{OH})_{5.95}]\text{Cl}_{0.71}(\text{OH})_{0.29} \cdot 1.48\text{H}_2\text{O}$ ) were placed in a 50-ml screw-tube and shaken at 10–60 °C for up to 60 min at 150 strokes per minute.

Assuming that only the  $\text{Cl}^-$  is exchanged for  $\text{SO}_4^{2-}$  in the interlayer of the HT, a stoichiometric quantity of HT-Cl should be regarded according to the following theoretical ion-exchange equation, replacing  $\text{Cl}^-$  for the  $\text{SO}_4^{2-}$ :



The pH of the suspended solution was measured after shaking, and the solids were filtered and washed with deionized water. The  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations were determined by ion chromatography as described in Section 2.1.

## 3. Results and discussion

### 3.1. Synthesis of HT-Cl

Fig. 1 shows the XRD patterns of HT-Cl, which has a chemical composition of  $[\text{Mg}_{1.98}\text{Al}(\text{OH})_{5.95}]\text{Cl}_{0.71}(\text{OH})_{0.29} \cdot 1.48\text{H}_2\text{O}$ . Since all of the XRD peaks of HT-Cl corresponded to those of hydrotalcite, the prepared HT-Cl was confirmed to have the structure of HT. The interlayer thickness of 2.95 Å was estimated by subtracting the brucite layer thickness 4.77 Å from the basal spacing ( $d_{006}$ ) 7.72 Å. The value of the basal spacing was slightly smaller than that of HT- $\text{CO}_3$  (7.84 Å) shown in JCPDS card 22-700. These calculated values were in good agreement with the reported interlayer spacing values of synthesized HT-Cl materials [7,9,16]. This suggests that the  $\text{Cl}^-$  is not only absorbed on the surface of the HT but also intercalated in the interlayer of the HT material.

Inside the structure of hydrotalcite-like compounds, the excess charge of the host layer is caused by  $\text{Al}^{3+}$  ions. To maintain a charge balance, the amount of  $\text{Al}^{3+}$  in the host layer must

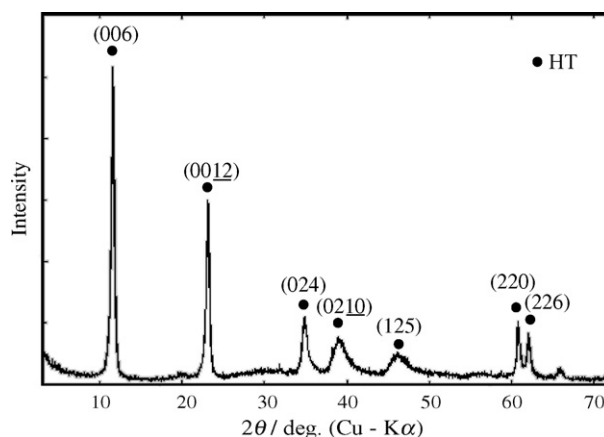


Fig. 1. X-ray powder diffraction pattern of the synthesized HT-Cl.

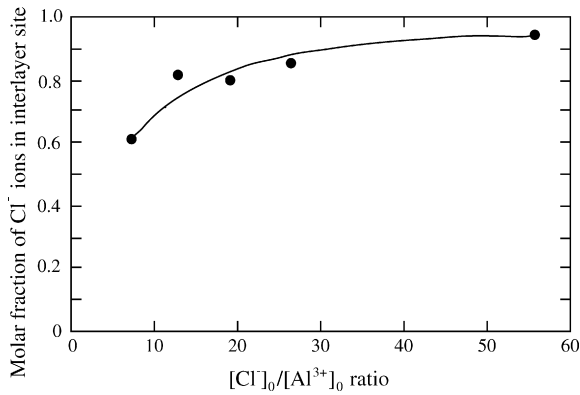


Fig. 2. Effect of the initial concentration ratio ( $[Cl^-]_0/[Al^{3+}]_0$ ) on the molar fraction of  $Cl^-$  in the interlayer site.

be proportional to the total equivalent of the anions in the interlayer. The  $[Cl^-]_0/[Al^{3+}]_0$  molar ratio of the preparation solution should affect the molar fraction of the  $Cl^-$  intercalated in the HT. The HT-Cl was prepared from varied  $[Cl^-]_0/[Al^{3+}]_0$  ratios in the solution under an excess  $[Cl^-]_0$  condition. The effect of the  $[Cl^-]_0/[Al^{3+}]_0$  ratio in solution on the molar fraction of the  $Cl^-$  in the interlayer is shown in Fig. 2.

The fraction of  $Cl^-$  in the interlayer site of the HT increased by raising the  $[Cl^-]_0/[Al^{3+}]_0$  molar ratio. When the concentration of  $Cl^-$  at the end of dripping of solution was 55 times more than required, all of the anions in the interlayer of HT could be exchanged by the  $Cl^-$ , yielding a 94% molar fraction of  $Cl^-$  in the HT interlayer. When the  $[Cl^-]_0/[Al^{3+}]_0$  molar ratio was between 13 and 26, the molar fraction of  $Cl^-$  was about 83%, and rarely changed.

The change in the molar fraction of the  $Cl^-$  intercalated in the HT was examined as a function of varying aging times for synthesizing HT-Cl, *i.e.*, from 1 to 24 h. A series of XRD patterns following various aging times and the change in the molar fraction of  $Cl^-$  in the interlayer site ( $x_{Cl}$ ) is shown in Fig. 3.

The molar fraction of  $Cl^-$  intercalated in HT increased as a function of longer aging times when the  $[Cl^-]_0/[Al^{3+}]_0$  molar

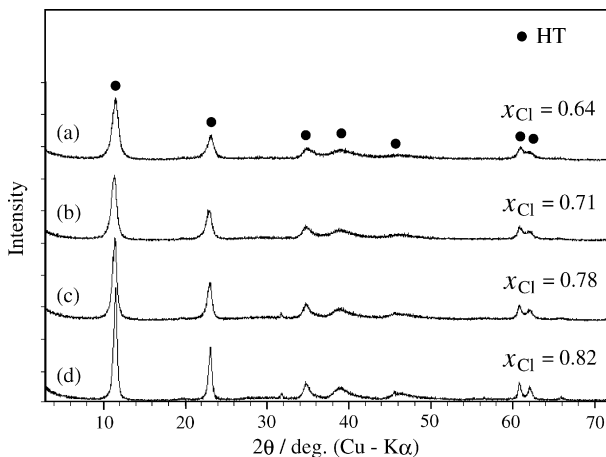


Fig. 3. XRD patterns of products as a function of aging time and the change in the molar fraction of  $Cl^-$  in the interlayer site ( $x_{Cl}$ ). The initial concentration ratio of  $[Cl^-]_0/[Al^{3+}]_0$  was 55. The curves represent: (a) 1 h, (b) 4 h, (c) 8 h, and (d) 24 h of aging time.

ratio was 55. The difference in the molar fraction of  $Cl^-$  according to an aging time between 1 and 24 h was about 18%. This result and that of the effect of the initial  $Cl^-$  concentration in solution suggest that not only  $Cl^-$ , but also  $OH^-$ , is intercalated in the HT during the preparation of HT-Cl; the  $OH^-$  in the interlayer of the HT may be exchanged with  $Cl^-$  in solution during aging. Equilibrium is achieved between the solution and interlayer site within a minimum of 24 h, and with a longer aging time, the HT-Cl material will become well crystallized. Thus, a minimum of 24 h of aging is required to prepare HT-Cl with a stable chemical composition.

When HT is prepared by the coprecipitation method, dripping the mixed  $MgCl_2-AlCl_3$  solution and the NaOH solution with a peristaltic pump, the pH of the suspension may change dramatically and locally since the solutions are added to the bulk solution drop-wise. In spite of preparing the HT under the same conditions, it is difficult to prepare the HT-Cl, which is of a fixed chemical composition, due to the local pH change in solution. Thus, two glass bars were placed between the injection ports for the added solutions and bulk solution in order to add solutions that were moving along the glass bars to the bulk solution continuously. As a result, the HT-Cl was synthesized three times with this method under the optimum conditions of a  $[Cl^-]_0/[Al^{3+}]_0$  molar ratio of 55 and aging time of 24 h. The HT-Cl material had an average  $Cl^-$  molar fraction of  $0.90 \pm 0.04$  (average  $\pm$  S.D.) in the interlayer of the HT, and an average Mg/Al molar ratio of 2.13.

### 3.2. $SO_4^{2-}$ removal by HT-Cl

Fig. 4 shows the effect of added HT-Cl on  $SO_4^{2-}$  removal. The ratio of added HT-Cl to the stoichiometric quantity varied from 0.2 to 2.7. The chemical compositions of the added HT-Cl were  $[Mg_{1.98}Al(OH)_{5.95}Cl_{0.71}(OH)_{0.29} \cdot 1.48H_2O]$  (Mg/Al molar ratio 2, theoretical sulfate ion-exchange capacity 3.0 meq./g-HT-Cl) and  $[Mg_{4.03}Al(OH)_{9.62}Cl_{0.80}(OH)_{0.20} \cdot 4.26H_2O]$  (Mg/Al molar ratio 4 and theoretical sulfate ion-exchange capacity 1.0 meq./g-HT-Cl). When HT-Cl with a Mg/Al molar ratio of 4 was added at 2.5 times above the

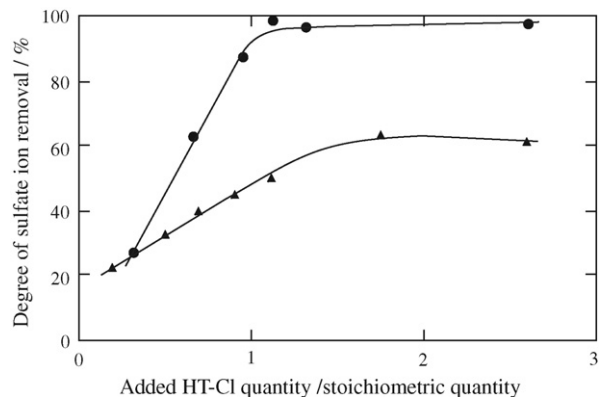


Fig. 4. The effects of adding HT-Cl on  $SO_4^{2-}$  removal. The time was 1 h, the temperature was  $25^\circ C$ , and the initial concentration of  $CaSO_4$  was 12 mM. HT-Cl with a Mg/Al molar ratio of 2 is depicted as a circle (●), and that with a molar ratio of 4 as a triangle (▲).

stoichiometric quantity in a  $\text{CaSO}_4$  solution, up to 60% of the  $\text{SO}_4^{2-}$  was removed. However, when HT-Cl with a Mg/Al molar ratio of 2 was added at 1.12 times above the stoichiometric quantity into a  $\text{CaSO}_4$  solution, about 99% of the  $\text{SO}_4^{2-}$  was removed. The sulfate ion adsorption capacity was 129 mg  $\text{SO}_4^{2-}$  per 1 g of HT-Cl, *i.e.*, 2.7 meq.  $\text{SO}_4^{2-}$  per 1 g of HT-Cl. It was thus confirmed that increasing the electrical charge density in the interlayer of the HT had the ability to strongly attract  $\text{SO}_4^{2-}$ .

The XRD patterns of the precipitates derived from the reaction of the  $\text{CaSO}_4$  solution with 1.12 times the stoichiometric quantity of the HT-Cl (Mg/Al molar ratio of 2) showed only the HT phase. This result suggests that anion exchange was achieved while maintaining the HT structure. The XRD peak of (006) was split in two after the ion-exchange reaction. It is assumed that more than one anion, of different ionic size, was intercalated inside the HT, thus supporting the premise that  $\text{SO}_4^{2-}$  was intercalated in the HT.

Fig. 5 shows the pH change in the reaction solution and the degree of dissolved  $\text{Mg}^{2+}$  from the HT-Cl material when 1.12 times the stoichiometric quantity of HT-Cl with a Mg/Al molar ratio of 2 was added to a 12 mM  $\text{CaSO}_4$  solution. With the addition of HT-Cl, the pH of the solution rose from 6.6 to 9.0, and the dissolved  $\text{Mg}^{2+}$  was detected in the reacted solution.

These results suggest that a part of the HT host layer dissolved into the solution. Since the concentration of  $\text{OH}^-$  increased following the dissolution of the host layer and competitive ion exchange between  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  occurred, it is thought that ion exchange did not progress according to the above stoichiometry. Fig. 6 shows the time course of  $\text{SO}_4^{2-}$  removal when 1.12 times the stoichiometric quantity of HT-Cl with a Mg/Al molar ratio of 2 was added to the 12 mM  $\text{CaSO}_4$  solution.

In the case of adding HT-Cl with a Mg/Al molar ratio of 2, we removed 99% of the  $\text{SO}_4^{2-}$  within 10 min of the addition. After the 10-min period, the removal rate of sulfate reached a plateau, indicating that the rate of ion exchange between HT-Cl and  $\text{SO}_4^{2-}$  was faster than the rate of removing  $\text{SO}_4^{2-}$  with Mg/Al oxides [17]. In the case of adding HT-Cl with a Mg/Al molar ratio of 4, nearly 50% of the  $\text{SO}_4^{2-}$  was removed after

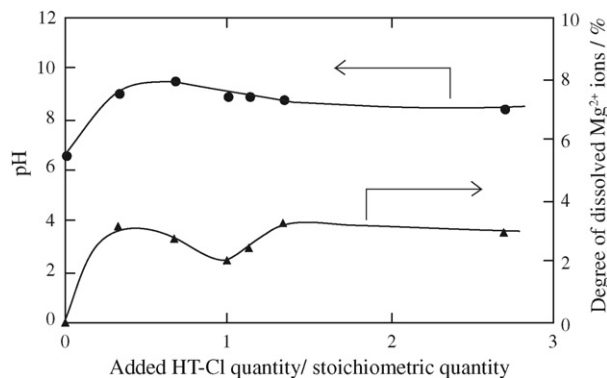


Fig. 5. The change in pH of the reaction solution and the degree of dissolved  $\text{Mg}^{2+}$  from HT-Cl with a time of 1 h. The temperature was 25 °C, the initial concentration of the  $\text{CaSO}_4$  was 12 mM, and the Mg/Al molar ratio was 2. The pH of the reaction solution is represented by a circle (●), and the degree of dissolved  $\text{Mg}^{2+}$  from the HT-Cl material is shown as a triangle (▲).

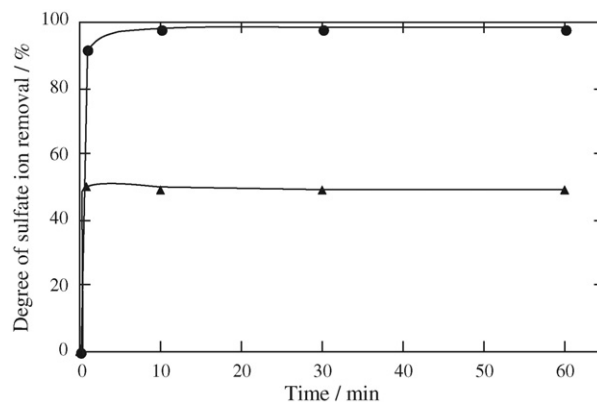


Fig. 6. The course of  $\text{SO}_4^{2-}$  removal as a function of time after HT-Cl was added. The HT-Cl quantity divided by the stoichiometric quantity was 1.12. The temperature was 25 °C and the initial concentration of the  $\text{CaSO}_4$  was 12 mM. HT-Cl with a Mg/Al molar ratio of 2 is depicted as a circle (●), and that with a molar ratio of 4 as a triangle (▲).

12 h, indicating that the removal rate of  $\text{SO}_4^{2-}$  mainly depends on the Mg/Al molar ratio within the HT-Cl material.

When 1.12 times the stoichiometric quantity of HT-Cl with a Mg/Al molar ratio of 2 was added to a solution containing 12 mM  $\text{CaSO}_4$ , and the temperature of the resulting solution was changed from 10 to 60 °C, over 88% of the  $\text{SO}_4^{2-}$  was removed after 1 h, independent of the temperature of the solution. A maximum of between 88 and 98% of the  $\text{SO}_4^{2-}$  was removed, regardless of the temperature of the solution.

When 1.12 times the stoichiometric quantity of HT-Cl with a Mg/Al molar ratio of 2 was added to a  $\text{CaSO}_4$  solution containing a concentration of  $\text{CaSO}_4$  at 1.2, 6, and 12 mM, the  $\text{SO}_4^{2-}$  removed after 1 h was 81, 90, and 98%, respectively. Increasing the initial concentration of  $\text{CaSO}_4$  in the solution caused the removal percentage of  $\text{SO}_4^{2-}$  to increase in small increments. Since the removal degree of  $\text{SO}_4^{2-}$  was over 80% at 1.2 mM  $\text{CaSO}_4$ , which is a dilute solution, HT-Cl could efficiently remove  $\text{SO}_4^{2-}$ . The concentration of  $\text{SO}_4^{2-}$  in landfill leachates is approximately a few millimolar [1]; therefore, we postulate that HT-Cl with a Mg/Al molar ratio of 2 will efficiently remove  $\text{SO}_4^{2-}$  in landfill leachate within this concentration. However, after treatment with HT-Cl, the residual sulfate concentrations are still not negligible, which can result in levels that can generate sulfide under anaerobic conditions.

The synthesized HT-Cl and resulting HT- $\text{SO}_4$  can produce HT- $\text{CO}_3$  with anion exchange in carbonate aqueous solution. Magnesium-aluminum oxide is obtained when the HT- $\text{CO}_3$  is heated to between 450 and 800 °C. This material can in turn intercalate anions in solution, reconstructing the HT-structure [17] so that it is recyclable. Since hydrotalcite is a clay mineral, it can be disposed of it in landfill.

#### 4. Conclusions

Hydrotalcite-like compounds intercalated with chloride ions in its interlayer site can be synthesized by a coprecipitation reaction. This coprecipitation reaction can generate a higher

concentration of chloride in the interlayer site, achieving the following results:

- The concentration ratio of chloride ions to aluminum ions ( $[Cl^-]_0/[Al^{3+}]_0$ ) in solution increased.
- The aging time should be sufficiently long for the anion-exchange material in solution to reach equilibrium.

Ion-exchange properties with  $SO_4^{2-}$  in solution were examined with synthesized HT-Cl, and we obtained following results:

- Adding 1.12 times the stoichiometric quantity of synthesized HT-Cl with a Mg/Al molar ratio of 2 to a solution containing 12 mM of calcium sulfate yielded approximately a 98% reduction in  $SO_4^{2-}$  within 10 min.
- The percent removal of  $SO_4^{2-}$  in solution was generally independent of the temperature and initial concentration of the  $SO_4^{2-}$  in solution.

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