

# Synthesis and adsorption properties of nanosized Mg–Al layered double hydroxides with $\text{Cl}^-$ , $\text{NO}_3^-$ or $\text{SO}_4^{2-}$ as interlayer anion

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Nanosized Mg–Al layered double hydroxides (LDHs) with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion have been synthesized by a modified coprecipitation method. The obtained LDHs were confirmed to be composed of a single phase and to be highly substituted by Al (Mg/Al ratio  $\sim 1.9$ ). The abilities of the LDHs to adsorb several harmful anions ( $\text{F}^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HAsO}_4^{2-}$  and  $\text{HSeO}_3^-$ ) in aqueous solution were studied. The LDHs exhibit high adsorption abilities. The amount of adsorption onto the LDHs differed between the starting interlayer anions, and decreased in the following order of the interlayer anions:  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . The  $\text{NO}_3^-$ -formed Mg–Al LDH reached a  $\text{CrO}_4^{2-}$  adsorption equilibrium state within only 30 min, much faster than those in previous reports. Thus, the nanocrystallized, highly Al substituted phase of the  $\text{NO}_3^-$ -formed Mg–Al LDH is found to markedly enhance the anion adsorption ability.

Keywords: *layered double hydroxides, nanocrystallization, anion adsorption, ion exchange, harmful anions*

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## 1. Introduction

The major sources of water pollution, which is one of the environmental issues that should be resolved, are industrial manufacturing processes. These processes discharge a large amount of industrial wastewater containing harmful elements that diffuse into the environment. Therefore, it is necessary to treat the wastewater prior to its discharge to the environment. Recently, numerous approaches have been studied for the development of economical and effective adsorbents for water pollutants [1–4]. Layered double hydroxides (LDHs) have attracted attention as a low-cost high-capacity adsorption material for harmful anions.

LDHs are a kind of synthetic anionic clay. The structure is based on brucite-like layers in which some divalent cations are partially replaced by trivalent ions, resulting in sheets with a positive charge [5, 6]. This charge is balanced by the intercalation of anions in hydrated interlayer regions. They can thus be considered complementary to aluminosilicate clays that have negatively charged sheets and interlayer cations. LDHs can be represented by the general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ . The identities of the di- and trivalent cations ( $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$ , respectively) and the interlayer anion ( $\text{A}^{n-}$ ) together with the value of the stoichiometric coefficient ( $x$ ) may be varied over a wide range, giving rise to a large class of isostructural materials. A typical material is the naturally occurring mineral hydrotalcite, which has the formula

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Table 1. Chemical compositions of synthesis solutions.

Samples	Mg source (g)	Al source (g)	NaOH (g)	Mg/Al ratio of synthesis solution
Cl-LDH	20.33	19.29	16	1.25
$\text{NO}_3$ -LDH	25.64	18.76	12	2
$\text{SO}_4$ -LDH	24.65	17.11	12	1.95

The Mg and Al sources are  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  for Cl-formed Mg–Al LDH,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  for  $\text{NO}_3$ -formed Mg–Al LDH, and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  for  $\text{SO}_4$ -formed Mg–Al LDH, respectively.

$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ; consequently, LDHs are also known as hydrotalcite-like materials. The interlayer anion is exchangeable and this property can be used to adsorb harmful anions polluting water and soil. Many researchers have studied the adsorption behavior of LDHs for the use in cleaning up environmental pollution [7–13].

$\text{CO}_3$ -formed Mg–Al LDH (hydrotalcite) is the most typical LDH, and its anion exchange properties have been studied for several decades. However, this carbonate is preferentially adsorbed and prevents significant anion exchange [14]. The calcination of Mg–Al LDHs produces intermediate nonstoichiometric oxides that undergo rehydration in aqueous media and yield hydroxide structures with different anions in interlayers (memory effect) [15]. This feature has been applied to the removal of harmful anions. Sato et al. showed that when heat-treated  $\text{CO}_3$ -formed Mg–Al LDH is added to an anion solution in excess,  $\text{HPO}_4^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{CrO}_4^{2-}$  are almost completely removed [14]. Studies of the removal from aqueous solutions of trichlorophenol [16], trinitrophenol [17–19], chromate, arsenate and vanadate [20, 21], and many other anions [22] have also been reported. Lazaridis et al. reported that the largest adsorption ability is achieved with LDHs calcined at 450 °C [23]. However, this method presents two shortcomings: (i) a complicated regeneration stage (the exhausted calcined material must be desorbed and recalcined at 400–500 °C for reuse) and (ii) an increase in solution pH.

The anion adsorption abilities of LDHs are affected considerably by Mg/Al molar ratio and the nature of the interlayer anions. Highly Al-substituted LDHs show a large capacity for anion adsorption [24]. The anion adsorption in LDHs by

anion exchange (intercalation) occurs when the interlayer anions are intercalated by weak electrostatic interactions with the layers, such as chloride or nitrate. Recently, we have reported that a nanosized hydrotalcite shows the high-efficiency adsorption of harmful anions [25]. In this study, highly Al-substituted and nanosized Mg–Al LDHs with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion were prepared by a modified coprecipitation method, and their adsorption abilities for several harmful anions were examined.

## 2. Experimental

### 2.1. Synthesis

Mg–Al LDHs with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  formed Mg–Al LDHs) were synthesized by a modified coprecipitation method at room temperature. Magnesium and aluminum salts (Junsei Chemical Co., Ltd.) were dissolved in 100 ml of  $\text{CO}_2$ -free distilled water at appropriate concentrations. 100 ml of NaOH (Junsei Chemical Co., Ltd.) solution at appropriate concentrations was added dropwise to 100 ml of a mixed salt solution with vigorous stirring. The chemical compositions of the prepared solutions are shown in Table 1. The aging time was approximately 1–2 min. The mixture was filtered and the solid phase was washed thoroughly with  $\text{CO}_2$ -free distilled water. Finally, the solids were dried at 50 °C for 24 h.

### 2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the samples were obtained using  $\text{CuK}\alpha$  radiation from a diffractometer (Rigaku, RINT-Ultima

Table 2. Morphological features and measured Mg/Al ratios of LDH samples.

Sample	$d_{003}$ (nm)	$d_{110}$ (nm)	Crystallite size along $c$ direction (nm)	Crystallite size along $a$ direction (nm)	Mg/Al ratio of obtained samples
Cl LDH	0.772	0.152	4.8	11.8	1.91
NO <sub>3</sub> LDH	0.835	0.152	3.2	10.2	1.84
SO <sub>4</sub> LDH	0.898	0.152	4.5	17.9	1.87

III). Elemental analysis was performed by an inductivity coupled plasma (ICP) emission spectrometer (Seiko, SPS4000) for metal ions in the samples to determine the Mg and Al contents.

### 2.3. Adsorption experiments

An adsorption experiment on several harmful anions ( $F^-$ ,  $CrO_4^{2-}$ ,  $HAsO_4^{2-}$  and  $HSeO_3^-$ ) was carried out at room temperature. The adsorption abilities of the synthesized Cl-, NO<sub>3</sub>- and SO<sub>4</sub>-formed Mg–Al LDHs were compared. Dilute solutions of  $F^-$  (50.3 ppm),  $CrO_4^{2-}$  (100.2 ppm),  $HAsO_4^{2-}$  (100.9 ppm) and  $HSeO_3^-$  (50.6 ppm) were prepared from 1000 ppm standard solutions for atomic adsorption analysis (Kanto Chemical Co., Inc.). The

sample (0.2 g) was added to the dilute solutions (100 ml) and stirred with a magnetic stirrer for 60 min. The solid particles from the mixtures were separated by filtration, and the concentrations of residual anions ( $F^-$  and  $CrO_4^{2-}$ ) in the filtrates were determined using a UV-Vis photometer (LANGE, LASA-100) for  $F^-$  and  $CrO_4^{2-}$ , and the ICP emission spectrometer for  $HAsO_4^{2-}$  and  $HSeO_3^-$  ions.

A time-dependent adsorption of  $CrO_4^{2-}$  on the Mg–Al LDHs was carried out at room temperature. A dilute solution (100.2 ppm) of  $CrO_4^{2-}$  was prepared from 1000 ppm standard solutions (Kanto Chemical Co., Inc.) for atomic adsorption analysis. The sample (0.2 g) was added to the dilute solution (100 ml) and stirred with a magnetic stirrer for different time intervals (1–60 min). The solid particles from the mixtures were separated by filtration and the concentration of residual  $CrO_4^{2-}$  in the filtrates was determined using the UV-Vis photometer.

## 3. Results and discussion

### 3.1. Characterization

The X-ray diffraction patterns of the prepared samples are shown in Fig. 1, which confirm the formation of a hydrotalcite-like structure in all the samples. The diffraction peaks are indexed according to the 3R symmetry [5, 26, 27]. No other phase was observed in the XRD patterns of the samples. The (110) and (113) peaks of the samples are markedly overlapped for Cl- and SO<sub>4</sub>-formed Mg–Al LDHs. Some morphological features and Mg/Al ratios of the LDH samples are shown in Table 2. To obtain the  $d_{110}$  and the crystallite size along  $a$  direction that are calculated from the (110) peak, the deconvolution of the two overlapped peaks of (110) and (113) is carried out [28]. The rank of the  $d_{003}$  agrees with the rank of the ionic size, i.e.,  $Cl^-$  (0.336 nm) <  $NO_3^-$  (0.400 nm) <  $SO_4^{2-}$

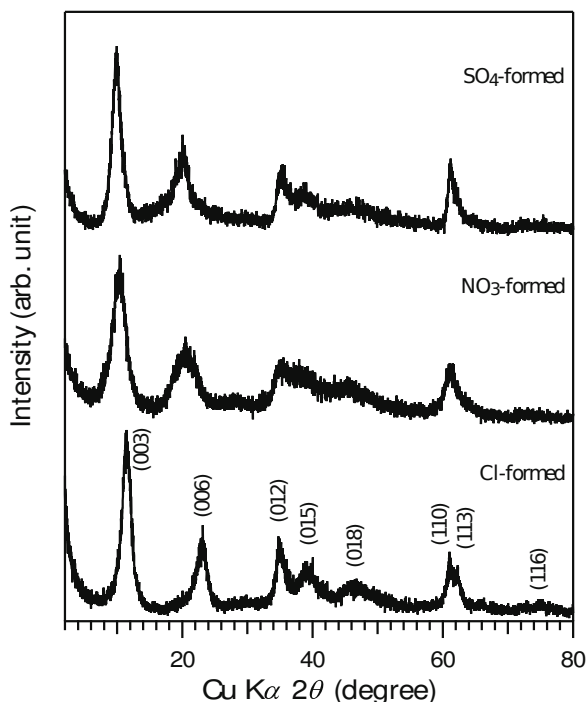


Fig. 1. XRD patterns of synthesized Mg–Al Cl-, NO<sub>3</sub>- and SO<sub>4</sub>-formed Mg–Al LDHs.

(0.436 nm) [29]. The  $d_{003}$  is substantially determined by the sum of the thickness of the basic layer and the size of the anion in the interlayer [30]. On the other hand, the three samples have the same size  $d_{110}$  value. Average crystallite sizes along  $c$  and  $a$  crystallographic directions were estimated by Scherrer's method using the XRD patterns of the (003) and (110) reflection of each sample. All the samples are smaller than 5 nm along  $c$  direction, although the crystallite sizes along  $a$  direction are in the range of 10–18 nm. The nanosized Mg–Al LDHs could be synthesized, because the crystal growth was suppressed by the short aging time (1–2 min).

The Mg/Al ratios of the obtained Cl-,  $\text{NO}_3^-$ - and  $\text{SO}_4$ -formed Mg–Al LDH are 1.91, 1.84 and 1.87, respectively. These show slightly low Mg/Al ratios. Generally, pure LDH phases can only be formed for stoichiometries in the range of  $2 \leq \text{M}^{\text{II}}/\text{M}^{\text{III}} \leq 4$  [5, 6]. It has been argued that for  $\text{M}^{\text{II}}/\text{M}^{\text{III}} < 2$ , the presence of  $\text{M}^{\text{III}}\text{--O--M}^{\text{III}}$  linkages is required, which is unfavorable from the point of view of charge repulsion (the so-called cation avoidance rule) [31–33]. However, there have been many claims that LDHs can be formed with stoichiometries outside the range of  $2 \leq \text{M}^{\text{II}}/\text{M}^{\text{III}} \leq 4$ , with reported  $\text{M}^{\text{II}}/\text{M}^{\text{III}}$  ratios as high as 13.3 for  $\text{CO}_3$ -formed Mg–Ga LDHs [34] and as low as 1.1 for  $\text{CO}_3$ -formed  $\text{M}^{\text{II}}\text{--M}^{\text{III}}$  LDHs ( $\text{M}^{\text{II}} = \text{Mg, Ni, Co, Cu}$ ;  $\text{M}^{\text{III}} = \text{Al, V}$ ) [24, 35–38] and 1.0 for  $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$  LDHs [39]. The elemental analysis of the metal content of a solid phase will give erroneous values if the LDH is mixed with  $\text{M}^{\text{III}}(\text{OH})_3$  or amorphous phase that might be expected to segregate when the synthesized mixture contains very low  $\text{M}^{\text{II}}/\text{M}^{\text{III}}$  ratios. Although  $\text{Al}(\text{OH})_3$  in gibbsite can be observed by XRD analysis at  $18.4^\circ$  as a secondary phase [28], no peak has been observed in the XRD patterns of the samples in this experiment. Furthermore, the absence of the by-product was confirmed by reported methods [40, 41]. It has been proposed that, if no change in Mg/Al ratio is observed after washing an Mg/Al LDH with hot NaOH, this can indicate the absence of amorphous aluminum oxy-species [40]. It has also been suggested that consistent values of the metal content in the bulk phase (e.g. as determined by ICP) and that of the sur-

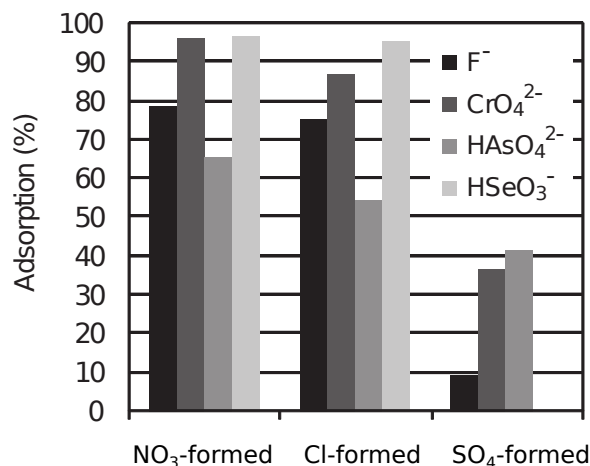


Fig. 2. Rates of adsorption of various harmful anions onto Cl-,  $\text{NO}_3^-$ - and  $\text{SO}_4$ -formed Mg–Al LDHs.

face (as determined by EDX) is a good evidence for the formation of a single LDH phase [41]. Therefore, highly Al substituted and nanosized Mg–Al LDHs with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion were successfully synthesized.

### 3.2. Adsorption of several harmful anions

To assess the adsorption ability of the obtained Mg–Al LDHs with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion, they were subjected to various anion adsorptions. The experimental results are shown in Fig. 2.  $\text{NO}_3$ -formed LDH adsorbed the highest amount of the anions among the three LDH samples. For example, the adsorption rates of  $\text{NO}_3$ -formed LDH, Cl-formed LDH and  $\text{SO}_4$ -formed LDH for  $\text{HAsO}_4^{2-}$  are 65.5, 54.7 and 41.3 %, respectively. The  $\text{HSeO}_3^-$ ,  $\text{SO}_4$ -formed LDH showed negligible adsorption ability. The adsorption ability of the nanosized LDHs was found to decrease in the following order of interlayer anions:  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . This order agrees with that of Mg–Al LDHs prepared by standard coprecipitation method, which was reported by Miyata [42]. This can be explained as the result of divalent anions interacting more strongly with brucite-like sheets than monovalent anions.

The variation of  $\text{CrO}_4^{2-}$  adsorption as a function of time is shown in Fig. 3. The kinetic curves show that the equilibrium times and adsorption capacities of nanosized Mg–Al LDHs with  $\text{Cl}^-$ ,  $\text{NO}_3^-$

and  $\text{SO}_4^{2-}$  as the interlayer anions are quite different. Using the  $\text{NO}_3$ -formed LDH as an adsorbent, the amount of removed  $\text{CrO}_4^{2-}$  exhibited the initial sharp increase ( $\sim 1$  min), after which it was rising slowly for 30 min. For this LDH, 30 min was necessary to reach the equilibrium, and the percentage of  $\text{CrO}_4^{2-}$  adsorption was 96.3 % at 60 min. For  $\text{Cl}$ -formed LDH and  $\text{SO}_4$ -formed LDH, both samples adsorbed about 20 %  $\text{CrO}_4^{2-}$  in the initial 1 min phase, and then the adsorption was rising gradually up to 60 min. The  $\text{CrO}_4^{2-}$  adsorption percentages at 60 min were 86.7 for  $\text{Cl}$ -formed LDH and 36.7 % for  $\text{SO}_4$ -formed LDH. This result suggests that a duration slightly longer than 60 min is necessary to reach the equilibrium state in  $\text{CrO}_4^{2-}$  adsorption on the two LDHs. The bends at 1 min are observed in all three curves, and this phenomenon can be explained by the following adsorption mechanisms. LDHs adsorb anions by two different mechanisms: (i) adsorption on the surface (fast) and (ii) ion exchange (slow) [13]. In the first minute, the fast anion adsorption is considered to be induced by the combined effect of the two adsorption mechanisms. The difference in adsorption equilibrium time between the interlayer anions are also explained by the strength of interaction with the brucite-like sheets. Generally, the anion adsorption onto LDHs by the anion-exchange method requires several hours or days [8, 43, 44]. Carriazo et al. reported that a  $\text{Cl}$ -formed  $\text{Mg}$ - $\text{Al}$  LDH prepared by standard coprecipitation method reached  $\text{CrO}_4^{2-}$  adsorption equilibrium after 7 days [43]. However, the  $\text{NO}_3$ -formed  $\text{Mg}$ - $\text{Al}$  LDH synthesized in this study required only 30 min to reach equilibrium. This result indicates that the nanocrystallization of  $\text{NO}_3$ -formed  $\text{Mg}$ - $\text{Al}$  LDH with the highly  $\text{Al}$  substituted phase markedly enhances the anion adsorption ability. Considering the simple synthesis and high anion adsorption capacities, the  $\text{NO}_3$ -formed  $\text{Mg}$ - $\text{Al}$  LDH has a high potential for the use as an effective adsorbent for water purification.

## 4. Conclusion

In this study,  $\text{Mg}$ - $\text{Al}$  layered double hydroxides (LDHs) with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  as the interlayer anion have been prepared by the modified copre-

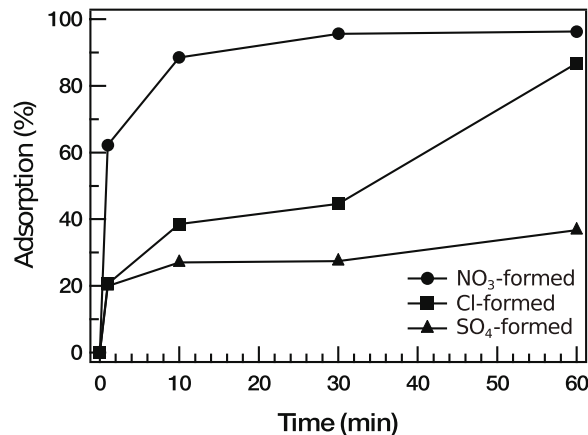


Fig. 3. Rates of adsorption of  $\text{CrO}_4^{2-}$  onto  $\text{Cl}$ -,  $\text{NO}_3$ - and  $\text{SO}_4$ -formed  $\text{Mg}$ - $\text{Al}$  LDHs as function of time.

cipitation method. The obtained LDHs were characterized by XRD analysis and ICP, which revealed their nanocrystalline structures and high  $\text{Al}$  content. A comparative study of the adsorption abilities of LDHs for several harmful anions ( $\text{F}^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HAsO}_4^{2-}$  and  $\text{HSeO}_3^-$ ) in aqueous solution was performed. The amount of adsorption onto the LDHs differed between the starting interlayer anions, and decreased in the following order of the interlayer anions:  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . Only 30 min was necessary for  $\text{NO}_3$ -formed  $\text{Mg}$ - $\text{Al}$  LDH to reach the equilibrium state in  $\text{CrO}_4^{2-}$  adsorption; this time was much shorter than those in previous reports, although the duration slightly longer than 60 min was necessary for  $\text{Cl}$ - and  $\text{SO}_4$ -formed  $\text{Mg}$ - $\text{Al}$  LDHs. The  $\text{NO}_3$ -formed  $\text{Mg}$ - $\text{Al}$  LDH was found to be the most effective adsorbent, and the nanocrystallized, highly  $\text{Al}$  substituted phase of the LDH was found to markedly enhance the anion adsorption ability.

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