



# Preparation of Mg–Al layered double hydroxide doped with Fe<sup>2+</sup> and its application to Cr(VI) removal



Tomohito Kameda\*, Eisuke Kondo, Toshiaki Yoshioka

Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

## ARTICLE INFO

### Article history:

Received 8 April 2013

Received in revised form 19 September 2013

Accepted 22 October 2013

Available online 31 October 2013

### Keywords:

Layered double hydroxide

Fe<sup>2+</sup>

Doping

Cr(VI)

Removal

## ABSTRACT

Mg–Al layered double hydroxide (Mg–Al LDH) doped with Fe<sup>2+</sup> was prepared by dropwise addition of a mixed solution of MgCl<sub>2</sub>, FeCl<sub>2</sub>, and AlCl<sub>3</sub> to NaOH solution at a constant pH. The Fe<sup>2+</sup>-doped LDH was found to be able to remove Cr(VI) from an aqueous solution through the anion exchange of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> with the intercalated Cl<sup>-</sup>, the production of Cr(OH)<sub>3</sub>, and the adsorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> on the surface of the produced FeO(OH). The excellent performance of this LDH for Cr(VI) removal is caused by both the anion exchange properties of Mg–Al LDH and the reducing activity of the Fe<sup>2+</sup> doped into the Mg–Al LDH. This process can be considered to occur through Langmuir-type adsorption, and the maximum adsorption amount and equilibrium adsorption constant are 12.5 mmol g<sup>-1</sup> and 242.1, respectively.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Layered double hydroxides (LDHs) are capable of anion exchange and thus have attracted attention as promising materials for applications such as water purification [1]. LDHs are typically represented by the formula [M<sub>1-x</sub><sup>2+</sup>M<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>](A<sup>n-</sup>)<sub>x/n</sub> · mH<sub>2</sub>O, where M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent metal ions, respectively, *x* denotes the M<sup>3+</sup>/(M<sup>2+</sup> + M<sup>3+</sup>) molar ratio (0.20 ≤ *x* ≤ 0.33), and A<sup>n-</sup> is, for example, CO<sub>3</sub><sup>2-</sup> or Cl<sup>-</sup> [2,3]. An LDH consists of a stack of M<sup>3+</sup>-bearing brucite-like octahedral layers in which the positive layer charge due to the replacement of some M<sup>2+</sup> with M<sup>3+</sup> is electrically neutralized by interlayer anions. The interlayer space is occupied by water molecules in the hydration shell of these intercalated anions.

Recently, Mg–Al LDH and the calcined Mg–Al oxide in particular have been investigated as promising materials for water preservation and purification. For example, these materials are able to take up oxometalates such as arsenite, arsenate, chromate, selenite, and selenate from aqueous solutions [4–14], and we have also examined the treatment of antimonate using these materials [15–17]. Furthermore, Fe–Al LDH that contains amorphous FeO(OH) and Al(OH)<sub>3</sub> was found to effectively remove Sb(V) from an aqueous

solution because of the anion exchange properties of the Fe–Al LDH and the adsorption of SbO<sub>3</sub><sup>-</sup> on the surface of the FeO(OH) [18].

Cr(VI) is present in the effluents from the electroplating, tanning, mining, and fertilizer industries [4], and the Cr(VI) wastewater must be treated in an environmentally acceptable manner. Depending on the pH of the environment, Cr(VI) is present as CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, which cannot be treated with alkaline agents to obtain Cr(VI) hydroxides. Therefore, Cr(VI) is first reduced to Cr(III) using a reducing agent, and the Cr(III) is treated with an alkaline agent to obtain Cr(OH)<sub>3</sub>. However, this treatment process is complicated, and the techniques can generate large amounts of sludge still contaminated with small amounts of Cr. Thus, the development of a new treatment method for aqueous solutions containing Cr(VI) is desired.

In this study, Mg–Al LDH doped with Fe<sup>2+</sup> was prepared by coprecipitation and used to remove Cr(VI) from an aqueous solution. Some Mg<sup>2+</sup> in the LDH host layer is expected to be replaced with Fe<sup>2+</sup>. Fig. 1 shows a schematic of the process for removing Cr(VI) with Fe<sup>2+</sup>-doped Mg–Al LDH. The Mg–Al LDH can take up Cr(VI) from an aqueous solution because of its anion exchange properties. The Cr(VI) is expected to be reduced to Cr(III) upon the oxidation of the Fe<sup>2+</sup> to Fe<sup>3+</sup>, and this Cr(III) combines with OH<sup>-</sup>, leading to the production of Cr(OH)<sub>3</sub>. Thus, the Fe<sup>2+</sup>-doped Mg–Al LDH is expected to remove Cr(VI) from an aqueous solution because of both the anion exchange properties of the Mg–Al LDH and the activity of the Fe<sup>2+</sup> as a reducing agent. Furthermore, an equilibrium study on the removal of Cr(VI) by the Fe<sup>2+</sup>-doped Mg–Al LDH was conducted.

Abbreviations: Mg–Al LDH, Mg–Al layered double hydroxide; XRD, X-ray diffraction; ICP–AES, inductively coupled plasma–atomic emission spectrometry; XPS, X-ray photoelectron spectroscopy.

\* Corresponding author. Tel./fax: +81 22 795 7212.

E-mail address: [kameda@env.che.tohoku.ac.jp](mailto:kameda@env.che.tohoku.ac.jp) (T. Kameda).

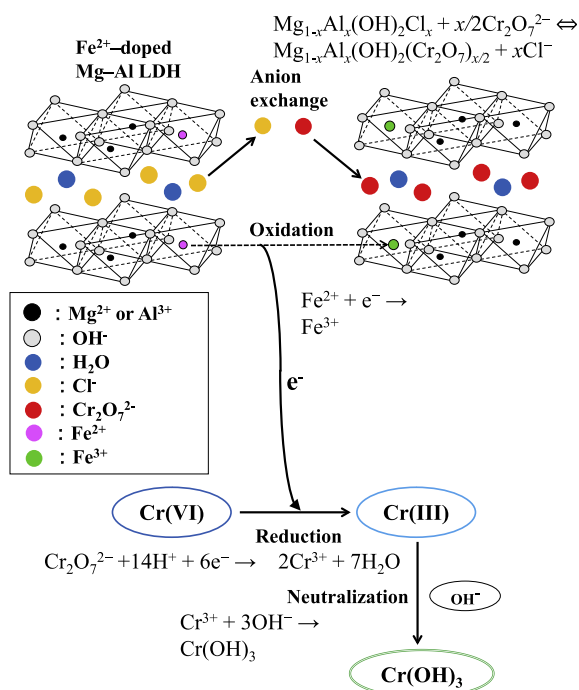


Fig. 1. Schematic of Cr(VI) treatment by Fe<sup>2+</sup>-doped Mg–Al LDH.

## 2. Experimental

All reagents were of chemical reagent grade and used without further purification.

### 2.1. Preparation of Mg–Al LDH doped with Fe<sup>2+</sup>

Mg–Al LDH doped with Fe<sup>2+</sup> was prepared by dropwise addition of Mg–Fe–Al solution to NaOH solution at constant pH. For comparison, Mg–Al LDH and Fe–Al LDH were also prepared. In total, four types of LDHs were prepared with Mg:Fe:Al molar ratios of 4:0:1, 3:1:1, 1:3:1, and 0:4:1. The four types of Mg–Fe–Al solutions, 0.4 mol/L Mg<sup>2+</sup> + 0.1 mol/L Al<sup>3+</sup>, 0.3 mol/L Mg<sup>2+</sup> + 0.1 mol/L Fe<sup>2+</sup> + 0.1 mol/L Al<sup>3+</sup>, 0.1 mol/L Mg<sup>2+</sup> + 0.3 mol/L Fe<sup>2+</sup> + 0.1 mol/L Al<sup>3+</sup>, and 0.4 mol/L Fe<sup>2+</sup> + 0.1 mol/L Al<sup>3+</sup>, were prepared by dissolving the required amounts of MgCl<sub>2</sub>, FeCl<sub>2</sub>, and AlCl<sub>3</sub> in 250 mL of deionized water. The NaOH solution (5 mol/L) was prepared by dissolving 100 g of NaOH in 500 mL of deionized water.

First, 250 mL of deionized water was poured into a flask, and N<sub>2</sub> was bubbled into the water for 30 min to degas it. The Mg–Fe–Al solution was then added dropwise to the deionized water at 10 mL/min and 30 °C, with stirring. The solution pH was adjusted to 10.5 by the addition of NaOH solution throughout the preparation. After adding the Mg–Fe–Al solution, the resultant suspension was kept standing at 30 °C for 1 h at a constant pH of 10.5. N<sub>2</sub> was bubbled into the solution throughout the procedure. The precipitate was recovered by filtering the resultant suspension and then repeatedly washed with deionized water and dried under reduced pressure (133 Pa) at 40 °C for 48 h.

The four types of LDHs prepared with Mg:Fe:Al molar ratios of 4:0:1, 3:1:1, 1:3:1, and 0:4:1 are hereafter called LDH 8Mg2Al-Cl, LDH 6Mg2Fe2Al-Cl, LDH 2Mg6Fe2Al-Cl, and LDH 8Fe2Al-Cl based on the nomenclature of the hydroxycarbonate supergroup [19].

### 2.2. Removal of Cr(VI) from an aqueous solution

The aqueous Cr(VI) solution containing Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions was prepared by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionized water. The four types of

LDHs were added to 500 mL of 1 mmol/L Cr(VI) solution, and the resultant suspension was kept standing at 30 °C for 120 min with stirring. N<sub>2</sub> was bubbled into the solution throughout the procedure. Samples of the suspension were withdrawn at different time intervals and immediately filtered through a 0.45-μm membrane filter. The filtrates were analyzed for residual Cr. The molar ratios of Al in the LDH to Cr(VI) in the solution (Al/Cr molar ratios) were set at 1–10. FeO(OH) was also used in this experiment as a reference material for its Cr(VI) adsorption capacity.

In order to find the adsorption isotherm of Cr(VI) adsorbed by LDH 6Mg2Fe2Al-Cl, Cr(VI) solution (20 mL of 0.1–20 mmol/L) and 0.2 g of the LDH 6Mg2Fe2Al-Cl were placed in 50-mL screw-top tubes and shaken at 30 °C for 24 h.

### 2.3. Characterization methods

The four types of LDHs before and after removal of Cr(VI) were analyzed by making X-ray diffraction (XRD) measurements using Cu Kα radiation. The LDHs were dissolved in 1 mol/L HCl and analyzed for Mg, Al, and Fe using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The LDHs before and after removal of Cr(VI) were also dissolved in 1 mol/L HCl, and the Fe<sup>2+</sup> concentration in the dissolved solution was determined by performing ultraviolet–visible spectrophotometry at 510 nm using the phenanthroline method. For the adsorption experiments, the residual concentrations of Cr in the filtrates were determined using ICP-AES. Furthermore, the oxidation state of Cr in LDH after removal of Cr(VI) was investigated using X-ray photoelectron spectroscopy (XPS).

## 3. Results and discussion

### 3.1. Preparation of Mg–Al LDH doped with Fe<sup>2+</sup>

Fig. 2 shows the XRD patterns for (a) LDH 8Mg2Al-Cl, (b) LDH 6Mg2Fe2Al-Cl, (c) LDH 2Mg6Fe2Al-Cl, and (d) LDH 8Fe2Al-Cl. The XRD peaks for all precipitates were attributable to hydroxycarbonate (JCPDS card 22-700), a naturally occurring hydroxycarbonate of magnesium and aluminum with the formula Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O and having the structure of a LDH. This suggests that all precipitates had the basic LDH structure. The peak intensity of the XRD patterns decreased in the order of LDH 8Mg2Al-Cl > LDH 6Mg2Fe2Al-Cl > LDH 2Mg6Fe2Al-Cl > LDH 8Fe2Al-Cl. This suggests the doping of Fe<sup>2+</sup> into the Mg–Al LDH host layer was successful for LDH 6Mg2Fe2Al-Cl and LDH 2Mg6Fe2Al-Cl. For LDH 8Fe2Al-Cl, the formation of LDH composed of Fe<sup>2+</sup> and Al<sup>3+</sup> is proposed. The observed basal spacing, *d*<sub>003</sub>, changed from 8.1 Å for LDH 6Mg2Fe2Al-Cl to 7.6 Å for LDH 2Mg6Fe2Al-Cl, because the amount

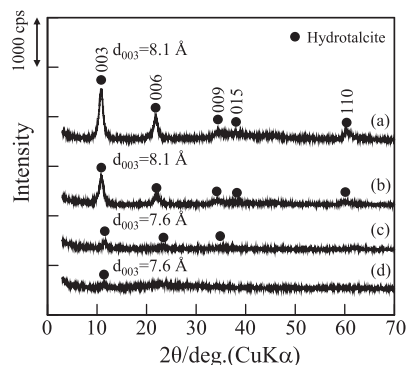


Fig. 2. XRD patterns for (a) LDH 8Mg2Al-Cl, (b) LDH 6Mg2Fe2Al-Cl, (c) LDH 2Mg6Fe2Al-Cl, and (d) LDH 8Fe2Al-Cl.

Download English Version:

<https://daneshyari.com/en/article/7044254>

Download Persian Version:

<https://daneshyari.com/article/7044254>

[Daneshyari.com](https://daneshyari.com)