Fluoride removal using calcined Mg/Al layered double hydroxides at high fluoride concentrations
Jae-Hyun Kim, Chang-Gu Lee, Jeong-Ann Park, Jin-Kyu Kang, Seo-Young Yoon and Song-Bae Kim

ABSTRACT
The aim of this study was to investigate the removal of high fluoride concentrations by Mg/Al layered double hydroxide (LDH). Batch experiments were conducted using calcined Mg/Al LDH at 105 °C (LDH-105), 300 °C (LDH-300), and 700 °C (LDH-700). The Brunauer-Emmett-Teller (BET) analysis showed that the specific surface area of LDH-700 was 1.7 – 1.8 times larger than those of LDH-105 and LDH-300. The X-ray diffractometry (XRD) analysis indicated that LDH-105 had a layered structure (Mg₄Al₂(OH)₁₂CO₃ · 3H₂O) while LDH-300 and LDH-700 were composed of mixed metal oxides (Al₈O₃N₆ + Mg₀.₄₄Al₀.₅₆) and magnesium oxide (MgO), respectively. Batch tests showed that the fluoride sorption capacity of LDH-700 was 1.7 – 2.9 times greater than those of LDH-105 and LDH-300 at initial fluoride concentrations of 100 and 200 mg/L. The kinetic data showed that fluoride sorption to LDH-700 arrived at equilibrium after 12 h. The equilibrium test demonstrated that the maximum sorption capacity of LDH-700 was 91.401 mg/g. Additional batch experiments indicated that the sorption capacity of LDH-700 decreased slightly when the solution pH was increased from 4.0 to 9.0. Moreover, fluoride sorption to LDH-700 decreased considerably in the presence of anions such as phosphate, sulfate, and carbonate in the following order: HPO₄²⁻ > SO₄²⁻ > CO₃²⁻ > Cl⁻ > NO₃⁻.

Key words | adsorbents, calcination, fluoride removal, Mg/Al layered double hydroxide, sorption

INTRODUCTION
Layered double hydroxides (LDHs) are a class of nanostructured anionic clays. They consist of positively charged brucite-like sheets that are balanced by the intercalation of anions in the hydrated interlayer regions (Goh et al. 2008). Because of the high surface area, large anion exchange capacity, and good thermal stability (Cavani et al. 1991), LDHs have been studied for their potential application in the removal of oxyanions, such as arsenate/arsenite, chromate, selenate/selenite, borate, and nitrate from contaminated waters (del Arco et al. 2000; Das et al. 2004; Gillman 2006; Islam & Patel 2009).

Fluoride contamination of drinking water resources is a serious environmental problem around the world. In many countries, fluoride occurs naturally in groundwater at concentrations exceeding the guidelines of the World Health Organization (1.5 mg/L), causing serious health problems. At concentrations greater than 1.5 mg/L, fluoride can cause neurological damage and dental/skeletal fluorosis (Ayoob & Gupta 2006). Adsorption is used widely for the removal of fluoride from water, primarily because of its cost effectiveness and simplicity of operation. Various adsorbents have been used for fluoride removal, including activated alumina, activated carbon, granular ferric hydroxide, limestone, fly ash, and clay (Bhatnagar et al. 2011).

LDHs have been used for fluoride removal by researchers (Das et al. 2003; Lv et al. 2007; Mandal & Mayadevi 2009; Batistella et al. 2011; Cai et al. 2012) in applications such as the removal of fluoride from aqueous solutions by
thermally treated Mg/Al LDH (Díaz-Nava et al. 2003) and the adsorption of fluoride to Zn/Al LDHs with different molar ratios of Zn/Al (Mandal & Mayadevi 2008), as well as in the use of Mg/Al/Fe LDH calcined at 500 °C as adsorbents for fluoride removal (Ma et al. 2011). The fluoride sorption capacities for LDH powders reported in the literature were in the range of 3.42–319.8 mg/g. High fluoride concentrations can be found in industrial wastewaters from glass-fertilizer, metal processing, and semiconductor industries (Lv et al. 2007). For instance, fluoride concentrations in the effluent from the electronic industry were in the range of 450–1,000 mg/L (Ndiaye et al. 2005). However, most of these studies were performed at low fluoride concentrations (5–20 mg/L) except the studies of Lv and his colleagues (Lv et al. 2006; Lv 2007; Lv et al. 2007) who conducted the experiments at fluoride concentrations of 50–1,500 mg/L. Further experiments are required to improve our knowledge regarding the performance of calcined LDHs in fluoride removal at high fluoride concentrations. The aim of this study was to investigate the removal of fluoride using calcined Mg/Al LDHs. Batch experiments were performed with a powder form of Mg/Al LDH under various conditions.

**MATERIALS AND METHODS**

**Preparation of Mg/Al LDH**

All chemicals used for the experiments were purchased from Sigma Aldrich. A powdered form of Mg-Al LDH was prepared by following the procedures of Han et al. (2011). The Mg/Al LDH powders were synthesized by co-precipitating mixtures of magnesium nitrate [Mg(NO₃)₂·6H₂O] and aluminum nitrate [Al(NO₃)₃·9H₂O]. A 700 mL solution (Mg/Al molar ratio = 2) of Mg(NO₃)₂·6H₂O (1 mol) and Al(NO₃)₃·9H₂O (0.5 mol) was added dropwise using a peristaltic pump (QG400, Fasco, Springfield, MO, USA) at 3 mL/min into 1,000 mL of alkali solution (pH = 13) consisting of sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) with intensive stirring at room temperature.

The resulting precipitates were aged at 65 °C for 18 h in mother liquor. The precipitates were washed thoroughly with deionized water to remove excess sodium, and then final suspensions were centrifuged at 8,500 rpm for 20 min. The washed precipitates were oven-dried again at 65 °C for 24 h and then pulverized in a ball mill. The pulverized precipitates were passed through US Standard Sieve No. 100 (grain size: 0.149 mm). The Mg/Al LDH used for the experiments was finally obtained via thermal treatment at 105 °C (LDH-105), 300 °C (LDH-300) and 700 °C (LDH-700) for 2 h in an electric muffle furnace (C-FMA, Vision Lab, Seoul, Korea). The mineralogical and crystalline structural properties were examined using X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) with a CuKα radiation of 1.5406 Å at a scanning speed of 0.6/sec. Surface areas were determined by BET N₂ adsorption analysis using an ASAP 2010 instrument (Micromeritics, USA).

**Fluoride adsorption experiments**

The desired fluoride solution was prepared by diluting the stocking fluoride solution (1,000 mg/L), which was made from sodium fluoride (NaF). First, batch experiments were performed using LDH-105, LDH-300 and LDH-700. LDH (0.2 g) was added to 50 mL of fluoride solution (initial concentration = 100 and 200 mg/L) in 50 mL polypropylene conical tubes. The tubes were shaken at 25 C and 100 rpm using a culture tube rotator (MG-150D, Mega Science, Korea). The samples were collected 24 h after the reaction and were filtered through a 0.45-μm membrane filter. The fluoride concentration was measured using a fluoride ion selective electrode (9609BNWP, Thermo Scientific, USA). For the fluoride measurement, total ionic strength adjustment buffer solution (58 g of NaCl, 57 mL of CH₃COOH, 150 mL of 6 M NaOH in 1,000 mL of deionized water) was used to prevent the interference of other ions.

Based on the results from the above tests, further batch experiments were conducted using LDH-700. To examine the effect of contact time on the fluoride removal, batch experiments were performed at the initial fluoride concentrations of 100 and 200 mg/L and an LDH dose of 0.2 g. In the experiments, the samples were collected 1, 2, 3, 6, 9, 12, and 24 h after the reaction. Next, equilibrium batch experiments were conducted at an initial fluoride concentration of 50–1,000 mg/L by adding 0.2 g of LDH to
30 mL of solution in 50 mL polypropylene conical tubes. The samples were collected 12 h after the reaction for the fluoride measurement. Further batch experiments were performed to examine the effect of LDH dosage on fluoride removal. The experiments were conducted at an initial fluoride concentration of 100 mg/L with LDH dosages ranging from 0.01 to 0.2 g in 30 mL of solution. In the pH experiments, the solution pH was adjusted to the desired value with 0.1 M NaOH and/or 0.1 M HCl. In the competing anion experiments, the competing anions (nitrate, chloride, phosphate, carbonate and sulfate) were added to the fluoride solution using Na-based chemicals (NaNO₃, NaCl, NaH₂PO₄, NaHCO₃, Na₂SO₄) to achieve the desired anion concentrations (5 and 50 mM). All experiments were performed in triplicate.

Data analysis

The kinetic model analysis can be performed using the following pseudo first-order and pseudo second-order models:

\[ q_t = q_e \left(1 - \exp(-k_1 t)\right) \]  
(1)

\[ \frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \]  
(2)

where \( q_t \) is the amount of fluoride removed at time \( t \), \( q_e \) is the amount of fluoride removed at equilibrium, \( k_1 \) is the pseudo first-order rate constant, and \( k_2 \) is the pseudo second-order velocity constant.

The equilibrium model analysis can be conducted using the following Langmuir and Freundlich isotherm models:

\[ q_e = \frac{Q_m K_L C}{1 + K_L C} \]  
(3)

\[ q_e = K_F C^n \]  
(4)

where \( C \) is the concentration of fluoride in the aqueous solution at equilibrium, \( K_L \) is the Langmuir constant related to the binding energy, \( Q_m \) is the maximum mass of fluoride removed per unit mass of LDH (maximum removal capacity), \( K_F \) is the distribution coefficient, and \( n \) is the Freundlich constant. Values of \( K_L \), \( Q_m \), \( K_F \), and \( n \) can be determined by fitting the Langmuir and Freundlich models to the observed data.

RESULTS AND DISCUSSION

Characteristics of calcined Mg/Al LDHs

The digital images and XRD patterns of calcined Mg/Al LDHs are presented in Figure 1, and the characteristics of calcined Mg/Al LDHs are summarized in Table 1. The colors of Mg/Al LDHs remained unchanged while XRD patterns changed during calcination. The LDH structure was preserved at 105°C. LDH-105 possessed reflection characteristics of a layered structure with sharp and intense lines at low 2\( \theta \) and less intense lines at high 2\( \theta \). LDH-105 had a chemical formula of Mg₄Al₂(OH)₁₂CO₃·3H₂O with a hexagonal crystal system. Meanwhile, the LDH phase was destroyed at 300°C and replaced by mixed metal oxides (Al₈O₃N₆ + Mg₀.₄₄Al₀.₅₆) with a hexagonal/rhombohedral crystal system. The LDH phase was also destroyed at 700°C to MgO with a cubic crystal system. The BET analysis indicated that the surface area of LDH-700 was 109.09 m²/g, which was 1.7–1.8 times larger than those of LDH-105 (60.76 m²/g) and LDH-300 (64.90 m²/g).

Fluoride removal by calcined Mg/Al LDHs

The fluoride adsorption capacities of calcined Mg/Al LDHs are compared in Figure 2. At an initial fluoride concentration of 100 mg/L, the adsorption capacity of LDH-700 was 14.9 mg/g, which was 2.5 and 1.7 times greater than those of LDH-105 (6.0 mg/g) and LDH-300 (8.7 mg/g), respectively. Moreover, the adsorption capacity of LDH-700 (28.4 mg/g) was 2.9 and 2.0 times greater than those of LDH-105 (9.8 mg/g) and LDH-300 (13.9 mg/g), respectively, at an initial fluoride concentration of 200 mg/L. The results indicated that the fluoride adsorption capacities of calcined Mg/Al LDHs were in the following order: LDH-700 > LDH-300 > LDH-105. This result could be attributed to the fact that calcination could alter the physical properties and chemical compositions of Mg/Al LDHs.
Wang et al. (2010) reported that the surface area of Mg/Al LDH calcined at 500°C was four times larger than that of Mg/Al LDH calcined at 130°C. They explained that the increase in surface area contributed to the increase in fluoride removal capacity of the LDH. Lv et al. (2006) also showed that the surface area of Mg/Al LDH changed as a result of thermal treatment, greatly affecting the percentage of fluoride removal.

In the removal of fluoride by LDH-105, two different removal mechanisms could be involved, surface adsorption and interlayer anion exchange. In surface adsorption, the negatively charged fluoride could adsorb to the positively charged brucite-like layer. Moreover, fluoride could replace the charge balancing anion (carbonate) in the interlayer.

Table 1 | Physical properties and chemical compositions of Mg/Al LDHs calcined at different temperatures

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Chemical composition</th>
<th>Crystal system</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>60.76</td>
<td>0.0302</td>
<td>Mg₄Al₂(OH)₁₂CO₃ ·3H₂O</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>300</td>
<td>64.90</td>
<td>0.0323</td>
<td>Al₆O₃N₆ + Mg₀.₄₄Al₀.₅₆</td>
<td>Hexagonal/Rhombohedral</td>
</tr>
<tr>
<td>700</td>
<td>109.59</td>
<td>0.0541</td>
<td>MgO</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

Figure 1 | Digital images and X-ray diffraction patterns for Mg/Al layered double hydroxides calcined at different temperatures.

Figure 2 | Fluoride adsorption capacities of calcined Mg/Al LDHs (initial fluoride concentrations – 100, 200 mg/L; LDH dose – 0.2 g/30 mL).
region via an anion exchange process (Goh et al. 2008). In LDH-300, fluoride could intercalate into the interlayer during the reconstruction/rehydration of the LDH-300 in an aqueous medium (reformation effect) (Lv et al. 2006). In addition, surface adsorption of fluoride to the mixed metal oxide phase could contribute to the removal of fluoride in LDH-300 (Fan et al. 2007). In the case of LDH-700, however, the LDH phase could not be reconstructed in the aqueous medium (Lv et al. 2006). Therefore, the reformation effect could not contribute to the fluoride removal in LDH-700, but the surface adsorption of fluoride to MgO could occur via the inner-sphere complex (Sasaki et al. 2011).

**Effects of contact time, initial fluoride concentration, and adsorbent dose**

The effect of contact time on fluoride removal in LDH-700 is shown in Figure 3. The fluoride concentrations decreased sharply with increasing contact time until the equilibrium was reached. At 3 h of reaction time, the fluoride concentrations were approximately 40–50% of the initial concentrations and decreased to 20–30% at 9 h. The fluoride sorption reached equilibrium by approximately 12 h of reaction time with fluoride concentrations of approximately 4–6% of the initial concentrations. After reaching the equilibrium, there were no significant changes in the fluoride concentrations.

The effect of the initial fluoride concentration on the removal of fluoride in LDH-700 is presented in Table 2. Fluoride removal was highly concentration dependent. At the lowest concentration of 50 mg/L, the removal percentage was approximately 98%, while the removal percentage decreased to 61% at the highest concentration of 1,000 mg/L. Meanwhile, the amount of fluoride removed increased from 6.8 to 93.7 mg/g with increasing fluoride concentrations from 50 to 1,000 mg/L. At lower concentrations, the fluoride ions available in the solution are fewer in number than the sorption sites on the adsorbents, but there are fewer sorption sites at higher fluoride concentrations.

The effect of adsorbent dose on fluoride sorption in LDH-700 (initial fluoride concentration = 100 mg/L) is shown in Figure 4. The removal percentage increased from 36.9 to 96.7% with increasing LDH doses from 0.01 to 0.2 g in 30 mL of solution. Meanwhile, the removal capacity of LDH-700 decreased from 109.5 to 14.3 mg/g with increasing adsorbent doses.

**Fluoride sorption kinetics and equilibrium isotherms**

The kinetics of fluoride removal in LDH-700 is shown in Figure 5. Model parameters for the pseudo first-order and pseudo second-order models obtained from the kinetic experiments are provided in Table 3. In the pseudo first-order model, the value of \( q_e \) at 100 mg/L of fluoride was 14.565 mg/g. At 200 mg/L, the value of \( q_e \) was 29.109 mg/g, which is about two times greater than that at 100 mg/L. The value of \( k_1 \) at 100 mg/L was 0.433 h\(^{-1}\), while it was 0.296 h\(^{-1}\) at 200 mg/L, indicating that the reaction rate at 100 mg/L was faster than that at 200 mg/L. The values of \( q_e \) from the pseudo second-order model were similar to those from the pseudo first-order model. At 100 mg/L,
the value of \( q_e \) was 16.420 mg/g, while it was 34.014 mg/g at 200 mg/L. The values of \( k_2 \) at 100 and 200 mg/L were 0.036 and 0.011 g/mg/h, respectively, indicating that the velocity constant at 100 mg/L was approximately three times greater than that at 200 mg/L. The correlation coefficients (\( R^2 \)) indicated that the pseudo second-order model described the kinetic data better than the pseudo first-order model.

The equilibrium isotherms of fluoride in LDH-700 are given in Figure 6, and the equilibrium isotherm constants are summarized in Table 4. In the Freundlich model, the distribution coefficient \( (K_F) \) was 12.903 L/g, while the Freundlich constant \( (n) \) was 0.338. In the Langmuir model, the Langmuir constant \( (K_L) \) was 0.043 L/mg, while the removal capacity \( (Q_m) \) was 91.401 mg/g, which was lower than those \( (213.2–319.8 \text{ mg/g}) \) of Lv and his colleagues \( (Lv \text{ et al.} \, 2006; \, Lv \, 2007; \, Lv \, et \, al. \, 2007) \) who performed the fluoride sorption experiments at high fluoride concentrations. However, our sorption capacity was in the range of the sorption capacity of LDH powders \( (3.42–319.8 \text{ mg/g}) \) reported in the literature. The correlation coefficient \( (R^2) \) of the Freundlich model was greater than that of the Langmuir model, indicating that the Freundlich isotherm appropriately described the experimental results.
Effects of solution pH and competing anions

The effect of solution pH on the removal of fluoride in LDH-700 (initial fluoride concentration = 100 mg/L) is shown in Figure 7. The fluoride adsorption capacity decreased slightly when the solution pH was increased from 4.0 to 9.0. The adsorption capacity was 15.6 mg/g at pH 4.0, decreasing to 14.1 mg/g at pH 9.0. The ligand exchange is known to be the main mechanism in the adsorption of fluoride to LDH-700 (MgO) surfaces (Sasaki et al. 2011). During the experiments, hydroxyl ions on the surfaces of LDH-700 are replaced by fluoride ions. At higher pHs, the concentration of hydroxyl ions increases with increasing pH, and thus, the competition between fluoride ions and hydroxyl ions to the adsorption sites of LDH-700 is enhanced.

The effect of anions on the removal of fluoride in LDH-700 (initial fluoride concentration = 100 mg/L) is presented in Figure 8. The monovalent anions nitrate (NO3−) and chloride (Cl−) had a low impact on the removal of fluoride at concentrations ranging from 5 to 50 mM. However, divalent anions such as sulfate (SO4^{2−}), phosphate (HPO4^{2−}), and carbonate (CO3^{2−}) greatly interfered with the removal of fluoride. Divalent anions are known to have a higher affinity for adsorbents than monovalent anions. Our results indicated that the removal of fluoride in LDH-700 was most affected by HPO4^{2−}. At the given experimental conditions, the order of the impact of the anions was HPO4^{2−} > SO4^{2−} > CO3^{2−} > Cl− > NO3−. Lv et al. (2006) reported that the order of the impact of anions on the fluoride removal was HPO4^{2−} > Cl− ≈ SO4^{2−} > NO3− in Mg/Al LDH thermally treated at 100 °C. In another study, Lv (2007) showed that the order of anion effect was HPO4^{2−} > SO4^{2−} > Cl− in Mg/Al LDH calcined at 500 °C.

CONCLUSIONS

The removal of high fluoride concentrations by Mg/Al LDHs was investigated using calcined LDHs (LDH-105, LDH-300, LDH-700). Batch tests showed that the fluoride sorption capacity of LDH-700 was 1.7–2.9 times greater than those of LDH-105 and LDH-300. The kinetic data showed that fluoride sorption to LDH-700 arrived at equilibrium after 12 h. The equilibrium test demonstrated that the maximum sorption capacity of LDH-700 was 91.401 mg/g. In addition, the fluoride sorption capacity of LDH-700 decreased slightly when the solution pH was increased from 4.0 to 9.0. Moreover, fluoride sorption to LDH-700 decreased considerably in the presence of anions (HPO4^{2−} > SO4^{2−} > CO3^{2−} > Cl− > NO3−). This study demonstrated that calcined Mg/Al LDHs could be used as adsorbents for the treatment of high fluoride solution.

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