Preparation of magnetic alginate–layered double hydroxide composite adsorbents and removal of Cr(VI) from aqueous solution
Chang-Gu Lee, Jeong-Ann Park, In Lee, Jin-Kyu Kang, Seo-Young Yoon and Song-Bae Kim

ABSTRACT
The aim of this study was to investigate the removal of Cr(VI) from aqueous solution using magnetic alginate–layered double hydroxide (LDH) composites. Magnetic iron oxide and calcined Mg-Al LDH powders were synthesized in the laboratory. The magnetic composites were prepared through immobilization of synthetic magnetic iron oxide and calcined Mg-Al LDH powders into an alginate matrix. The magnetic composites had a particle size of 1.5 ± 0.1 mm and showed magnetic properties under an external magnetic field. Results demonstrated that the magnetic composites were effective in the removal of Cr(VI). In the magnetic composites, calcined Mg-Al LDH played a major role in the sorption of Cr(VI), whereas magnetic iron oxide provided the magnetic property along with a minor role in Cr(VI) sorption. Kinetic tests showed that Cr(VI) sorption to the magnetic composites reached equilibrium at 24 h. The maximum Cr(VI) removal capacity was 11.15 mg/g. Results also indicated that Cr(VI) removal was not sensitive to solution pH between 4.1 and 9.5. This study demonstrated the potential applications of magnetic alginate–LDH composites for chromate removal from aqueous solution in combination with magnetic separation.

Key words | calcined layered double hydroxide, chromium sorption, magnetic alginate–LDH composites, magnetic iron oxide

INTRODUCTION
Chromium can exist in oxidation states ranging from −2 to +6. In aquatic environments, trivalent Cr(III) and hexavalent Cr (VI) are the major forms of chromium, and Cr(VI) is more toxic and cancerous (Zhitkovich 2011). Chromium contamination of drinking water resources is a serious global environmental problem. In many countries, chromium is present in groundwater at concentrations exceeding the guidelines of the World Health Organization (0.05 mg/L), causing serious health problems (Richard & Bourg 1999). Various treatment methods have been used for the removal of chromium from water, including coagulation-precipitation, ion exchange, adsorption, and membrane technology. Adsorption can be widely used for chromium removal because of cost-effectiveness and simplicity of operation (Sharma et al. 2011).

Magnetic separation is an innovative technology and has been applied by several researchers to water treatment and purification (Yavuz et al. 2009). For magnetic separation, magnetic particles such as magnetite (Fe3O4) and maghemite (γ-Fe2O3) are immobilized into polymers such as alginate, chitosan, polyvinyl alcohol, and gellan gum to form magnetic beads or composites (Yavuz et al. 2009). In addition, functional materials are added into the beads/composites to remove target contaminants. Along these lines, recent studies have focused on recovery of Cr(VI) from wastewater using magnetic beads containing Rhizopus cohnii (industrial fungus) (Li et al. 2008), adsorption of Cr(III) to magnetic gellan gum beads (Wang et al. 2009), photocatalytic reduction of Cr(VI) to Cr(III) using maghemite-containing
magnetic beads (Idris et al. 2011), and separation of Cr(VI) from an aqueous solution using magnetic chitosan beads modified with diethylenetriamine (Li et al. 2011).

Layered double hydroxides (LDHs) are a class of nano-structured 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). LDHs have high surface areas, large anion exchange capacities, and good thermal properties (Cavani et al. 1991). Several researchers have investigated the adsorption and removal of Cr(VI) using various LDHs (Prasanna et al. 2006; Tzou et al. 2007; Prasanna & Kamath 2008; Goh & Lim 2010). They have observed the removal of Cr (VI) using calcined Mg-Al LDH through an anion exchange reaction between a chromate ion and a hydroxyl ion (Rhee et al. 1997), better performance of chloride-LDH as adsorbents than calcined carbonate LDH in Cr(VI) removal (Carriazo et al. 2007), Cr(VI) removal by Mg-Al LDH nanoparticles (Goh et al. 2010), and the influence of textural and structural properties of calcined Mg-Al and Mg-Zn-Al LDHs on sorption of Cr(VI) (Dudek et al. 2012). To our knowledge, however, studies related to the removal of Cr(VI) by magnetic composites containing LDHs are scarce.

The aim of this study was to investigate the removal of Cr(VI) from aqueous solution using magnetic alginate-LDH composites. The magnetic composites were prepared through immobilization of synthetic magnetic iron oxide and calcined Mg-Al LDH powders into an alginate matrix. Then, batch experiments were performed under various experimental conditions to examine the removal of Cr(VI) by the magnetic composites.

### MATERIALS AND METHODS

#### Preparation of magnetic iron oxide and calcined Mg-Al LDH

All chemicals used for the experiments were purchased from Sigma Aldrich. Magnetic iron oxide particles were prepared by co-precipitating a solution of iron sulfate (FeSO₄·7H₂O) and iron chloride (FeCl₃·6H₂O). An alkali solution of sodium hydroxide (NaOH) was added drop wise into a 500 mL solution of FeSO₄·7H₂O (0.125 mol) and FeCl₃·6H₂O (0.25 mol) with intensive stirring at room temperature until pH 8.0 was reached. The resulting precipitates were aged at 60 °C for 18 h and then washed thoroughly with deionized water to remove excess sodium. The washed precipitates were oven-dried at 150 °C for 6 h and then pulverized in a ball mill.

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 drop wise into 1,000 mL of an alkali solution (pH = 13) of sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) using a peristaltic pump (QG400, Fasco, Springfield, MO, USA) at 3 mL/min under intensive stirring at room temperature. The resulting precipitates were aged at 65 °C for 18 h in the mother liquor. The precipitates were washed thoroughly with deionized water to remove excess sodium. Then, final suspensions were centrifuged at 11,200 × g (8,500 rpm) for 20 min. The washed precipitates were oven-dried again at 65 °C for 24 h and were then pulverized in a ball mill. The calcined Mg-Al LDH used for the experiments was finally obtained via thermal treatment at 300 °C for 24 h in an electric muffle furnace (C-FMA, Vision Lab, Seoul, Korea). The previous experiments showed that the Mg-Al LDH calcined at 300 °C had a higher BET surface area and total pore volume than the untreated LDH (Kim et al. 2022). Mineralogical and crystalline structural properties of magnetic iron oxide and calcined Mg-Al LDH were examined using X-ray diffractometry (XRD, D8 Advance, Bruker, Germany) with CuKα radiation at 1.5406 Å at a scanning speed of 0.6°/s.

#### Preparation of magnetic alginate–LDH composites

Magnetic alginate–LDH composites were prepared by entrapping powdered forms of both calcined Mg-Al LDH and magnetic iron oxide in an alginate hydrogel. One gram of sodium alginate powder was added to 100 mL deionized water to prepare a sodium alginate solution at room temperature. Then, the desired amount of calcined LDH and magnetic iron oxide (8% w/v; for instance, 6 g calcined LDH + 2 g magnetic iron oxide) were added to 100 mL of an alginate solution under intensive stirring to obtain a homogeneous suspension. ‘8% w/v’ was used to synthesize...
the magnetic composites because a higher percentage (>8%) was found to cause clogging at the outlet of the scalp vein set during synthesis. The suspension was allowed to drop using a disposable scalp vein set (needle diameter = 0.7 mm) equipped with a syringe pump (78-1100I, Fisher Scientific) at 4 mL/min into a stirred reservoir containing 200 mL of a 0.3 M calcium chloride (CaCl₂) solution. The resulting composites were allowed to cure in the same CaCl₂ solution for 24 h under stirring and for another 24 h without stirring. Then the magnetic composites were rinsed with deionized water to remove any excess Ca²⁺. Prior to use, the magnetic composites were dried in an oven at 60°C for 24 h. The chemical composition of the magnetic composites was investigated using an X-ray fluorescence spectrometer (XRF, S4 pioneer, Bruker, Germany). The surface area, total pore volume and average pore diameter of the magnetic composites were measured by N₂ adsorption-desorption isotherms and Barrett-Joyner-Halenda analysis using a surface area analyzer (BELSORP-max, BEL Japan Inc., Japan).

Batch experiments

The desired Cr(VI) solution was prepared by diluting the stock Cr(VI) solution (1,000 mg/L), which was made from potassium dichromate (K₂Cr₂O₇). All batch experiments were performed in 50 mL polystyrene conical tubes. Batch experiments were conducted to examine Cr(VI) removal by the magnetic composites composed of different contents of calcined LDH and magnetic iron oxide (8–0%, 6–2%, 4–4%, 2–6%). The experiments were conducted at an initial Cr(VI) concentration of 10 mg/L with a composite dose of 0.05 g in 30 mL solution. As a background electrolyte, 20 mM potassium nitrate (KNO₃) was used in the experiments. The tubes were shaken at 25°C and 100 rpm using a shaking incubator (Daihan Science, Korea). Then the magnetic composites were separated from the solution using a magnet (≈1.18 Tesla) 24 h post-reaction. The Cr(VI) concentration was measured using the diphenylcarbazide method.

Next, kinetic batch experiments were performed at the initial Cr(VI) concentration of 10 mg/L and a composite dose of 0.05 g in 30 mL solution. In the experiments, samples were collected at 2, 4, 8, 12, 24, 36 and 48 h post-reaction. Equilibrium batch experiments were conducted with different concentrations of Cr(VI) solution. Magnetic composite (0.05 g) was added to 30 mL of a chromate solution (initial concentration = 5–200 mg/L). The samples were collected 24 h post-reaction. In the pH experiments, 0.1 M NaOH and 0.1 M HCl solutions were used to adjust pH from 4.1 to 9.5. The pH was measured with a pH probe (9107BN, Thermo Scientific, USA). All experiments were performed in triplicate.

Data analysis

The kinetic data were analyzed using the following pseudo first-order and pseudo second-order models:

\[ Q_t = q_e [1 - \exp(-k_1t)] \]  
\[ Q_t = \frac{K_2q^2 e t}{1 + K_2q e t} \]  

where \( q_t \) is the amount of Cr(VI) removed at time \( t \) (mg/g), \( q_e \) is the amount of Cr(VI) removed at equilibrium (mg/g), \( k_1 \) is the pseudo first-order rate constant (1/h), and \( k_2 \) is the pseudo second-order velocity constant (g/mg/h). In addition, the kinetic data were analyzed with the following intra-particle diffusion model (Weber–Morris equation) (Bajpai & Armo 2009):

\[ q_t = k_i t^{1/2} + I \]

where \( k_i \) is the intra-particle diffusion rate constant (mg/g/h^{1/2}), and \( I \) is the intercept (mg/g) related to the thickness of the boundary layer.

The equilibrium data were analyzed using the following Langmuir and Freundlich isotherm models:

\[ q_e = \frac{Q_m K_L C}{1 + K_L C} \]  
\[ q_e = K_F C^n \]

where \( C \) is the concentration of Cr(VI) in the aqueous solution at equilibrium (mg/L), \( K_i \) is the Langmuir constant related to the binding energy (L/mg), \( Q_m \) is the maximum
mass of Cr(VI) removed per unit mass of the magnetic composites (removal capacity) (mg/g), $K_F$ is the distribution coefficient (L/g), 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.

Mean separations were performed on the data from the pH experiment using Tukey’s Honestly Significant Difference test. The statistical analysis was performed using SAS version 9.1 and differences were considered significant at $p < 0.05$.

### RESULTS AND DISCUSSION

#### Characteristics of magnetic alginate–LDH composites

Magnetic alginate–LDH composites used in the experiments are shown in Figure 1. They had magnetic properties under an external magnetic field (Figure 1(a)). XRD data showed that calcined Mg-Al LDH had a sharp and intense line at low $2\theta$ and less intense lines at high $2\theta$ (Figure 1(b)) with the peaks corresponding to LDH (JCPDS 53-0005, $2\theta = 26.939, 33.833, 36.371, 43.704, 60.188, 61.847$), which conformed well with the literature (Kanezaki 1998). The calcined Mg-Al LDH had a chemical composition of Mg0.7Al0.28(OH)1.98(CO3)0.15 0.48H2O. The XRD pattern of magnetic iron oxide indicated the peaks corresponding to maghemite ($\gamma$-Fe2O3, JCPDS 89-5892, $2\theta = 30.266, 35.651, 43.332, 53.766, 57.319, 62.949$) and goethite ($\alpha$-FeOOH, JCPDS 81-0464, $2\theta = 21.240, 33.243, 41.183, 58.998$). The magnetic composites had a particle size of $1.5 \pm 0.1$ mm. They had the BET specific surface area of 73.3 $m^2/g$ and total pore volume of 0.248 $cm^3/g$ (Table 1). The chemical composition from XRF analysis (Table 2) indicated that the magnetic composites were composed of C/H (53.0%), Mg (22.4%), Al (12.7%), Fe (9.2%), and Ca (2.7%). Note that C/H and Ca came from the alginate matrix, whereas Mg and Al came from calcined LDH and Fe from magnetic iron oxide.

#### Cr(VI) removal by magnetic alginate–LDH composites

Cr(VI) removal at various contents of calcined LDH–magnetic iron oxide in the magnetic composites is shown in Figure 2. For experiments with no added iron oxide (8% calcined LDH–0% magnetic iron oxide, MC-80), the adsorption capacity of the composites (MC-80) was 2.17 mg/g. At an iron oxide content of 2% (6% calcined LDH–2% magnetic iron oxide, MC-62), the capacity of

| Physical characteristics of magnetic alginate–LDH composites used in the experiments |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Particle size (mm)              | BET surface area (m²/g)         | Total pore volume (cm³/g)       | Mesopore volume (cm³/g)         | Micropore volume (cm³/g)        | Average pore diameter (nm)      |
| 1.5 ± 0.1                       | 73.3                            | 0.248                           | 0.241                           | 0.007                           | 13.5                            |

| Chemical composition of magnetic alginate–LDH composites before and after Cr (VI) sorption experiments (data from XRF analysis) |
|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Chemical compositions (weight %)                | CHO                            | MgO                            | Al₂O₃                          | Fe₂O₃                          | CaO                            | K₂O                            | Cr₂O₃                          | Total                          |
| Before                                         | 53.0                           | 22.4                           | 12.7                           | 9.2                            | 2.7                            | -                              | -                              | 100                            |
| After                                          | 42.0                           | 25.6                           | 15.5                           | 13.0                           | 2.6                            | 1.0                            | 0.3                            | 100                            |
MC-62 was reduced to 1.50 mg/g. When the iron oxide content increased from 2 to 4% (4% calcined LDH–4% magnetic iron oxide, MC-44), the capacity of MC-44 decreased further to 1.31 mg/g. Another 2% increase in the iron oxide content from 4 to 6% (2% calcined LDH–6% magnetic iron oxide, MC-26) resulted in a decrease of the adsorption capacity of MC-26 to 0.98 mg/g. These results demonstrated that the Cr(VI) sorption capacity of the composites decreased with decreasing calcined LDH (increasing magnetic iron oxide) content in the composites. Note that the sorption capacity of MC-26 was only 66% of the MC-62 capacity in given experimental conditions. This indicated that calcined LDH played a major role in the sorption of Cr(VI), whereas magnetic iron oxide provided the magnetic property along with a minor role in Cr(VI) sorption. For further experiments, the composites with 6% calcined LDH and 2% magnetic iron oxide were used.

Cr(VI) removal upon repeated use of the magnetic composites (adsorbent dose = 0.05 g; initial Cr(VI) concentration = 10 mg/L) is presented in Figure 3. Through magnetic separation, the composites were used repeatedly for Cr(VI) removal. For each round of the test, the composites were removed from the solution at 24 h post-reaction using a magnet, moved to deionized water for a 4-h stay, and then applied to a new Cr(VI) solution (concentration = 10 mg/L). In the first use, the Cr(VI) adsorption capacity was determined to be 1.61 mg/g. After the first use, the XRF analysis was performed for the magnetic composites, indicating the presence of Cr on the adsorbent (Table 2). Note that K detected on the adsorbent came from potassium dichromate (K$_2$Cr$_2$O$_7$) used to prepare the Cr(VI) solution. In the second round, the adsorption capacity was reduced to 0.61 mg/g. The adsorption capacity was reduced to 0.42 mg/g in the third round, and was absent in the fourth round.

In our experiments, chromate ions (HCrO$_4$ $^-$, Cr$_2$O$_7^{2-}$) in aqueous solution could diffuse into the magnetic composites through the pores of the composites. Then, chromate ions could come in contact with the entrapped particles and subsequently be removed from the aqueous phase to the solid phase. In surface adsorption, the negatively charged chromate could adsorb to the positively charged brucite-like layer (Prasanna et al. 2006). Chromate ions could replace the charge balancing anion (carbonate) in the interlayer region of LDHs via an anion exchange process (Goswamee et al. 1998). Furthermore, chromate could intercalate into the interlayer during the reconstruction/rehydration of the calcined LDH in an aqueous medium (Rhee et al. 1997). In addition, some of the chromate ions could adsorb to magnetic iron oxide particles through electrostatic interaction and anion exchange (Hu et al. 2005).

Characteristics of Cr(VI) removal by magnetic alginate–LDH composites

The kinetics of Cr(VI) adsorption by the magnetic composites is provided in Figure 4. The adsorption reached equilibrium around 24 h of reaction time. In the pseudo first-order model, the value of $q_e$ was 1.51 mg/g while the value of $k_1$ was 0.311/h. In the pseudo second-order
model, the value of $q_e$ was 1.64 mg/g while the value of $k_2$ was 0.27 g/mg/h. The value of $q_e$ from the pseudo second-order model was greater than that from the pseudo first-order model. Correlation coefficients ($R^2$) indicated that both the pseudo first-order model ($R^2 = 1.00$) and pseudo second-order model ($R^2 = 0.99$) described the kinetic data properly.

An intra-particle diffusion model applied to the kinetic sorption data is shown in Figure 5, indicating that the plots were composed of two line segments. The diffusion model was well fitted to the data, with coefficients of determination ($R^2$) of 0.99 (first line) and 0.95 (second line). Values of $k_i$ for the first and second lines were 0.46 and 0.02 mg/g/h$^{1/2}$, respectively. The first line in the plot indicates boundary layer adsorption, while the second line describes the intra-particle diffusion (Bajpai & Armo 2009).

The equilibrium isotherm of Cr(VI) sorption by the composites is illustrated in Figure 6. In the Freundlich model, the distribution coefficient ($K_F$) was 0.39 L/g while the Freundlich constant ($n$) was 0.55. In the Langmuir model, the Langmuir constant ($K_L$) was 0.01 L/mg while the maximum removal capacity ($Q_m$) was 11.15 mg/g. The correlation coefficient ($R^2$) of the Freundlich model ($=0.99$) was greater than that of the Langmuir model ($=0.94$). The maximum adsorption capacity determined from our experiments (11.15 mg per gram of the magnetic composites) was in the range of the chromate removal capacity for LDHs (9–160 mg/g) reported in the literature (Goh et al. 2008).

The effect of initial solution pH on Cr(VI) removal by the composites is presented in Figure 7. Adsorption capacity was 1.65 mg/g at pH 4.1 and increased slightly to 1.82 mg/g at pH 5.8. As the solution pH further increased, the adsorption capacity decreased slightly and arrived at 1.56 mg/g at pH 9.5. These results demonstrated that Cr(VI) removal in the composites was not drastically changed in the pH range of 4.1–9.5. This could be related to the fact that the final (equilibrium) pH converged to 8.2–8.3 in the experiments. The effect of initial solution pH was minimized due to a change of solution pH, and so the adsorption capacities of the composite at pH 4.1–9.5 were not significantly different. Our results were similar with those of a previous report (Rocher et al. 2008) showing that the removal of organic dyes in magnetic alginate beads containing activated carbon was not affected by solution pH between 3 and 10. It was also reported that
CONCLUSIONS

In this study, the removal of Cr(VI) by magnetic alginate-LDH composites was examined. Results demonstrated that the magnetic composites were effective in the removal of Cr(VI). In the composites, calcined LDH played a major role in the sorption of Cr(VI), whereas magnetic iron oxide provided the magnetic property along with a minor role in Cr(VI) sorption. Kinetic tests showed that Cr(VI) sorption to the composites reached equilibrium at 24 h. The maximum Cr(VI) removal capacity was determined to be 11.15 mg/g. Results also indicated that Cr(VI) removal was not sensitive to initial solution pH between 4.1 and 9.5. This study demonstrated potential applications of magnetic alginate-LDH composites for chromate removal from aqueous solution in combination with magnetic separation.

ACKNOWLEDGEMENT

This research was supported by the National Research Foundation of Korea, funded by the Ministry of Education, Science and Technology, Republic of Korea (grant number 2012-0001296).

REFERENCES


Li, H., Bi, S., Liu, L., Dong, W. & Wang, X. 2011 Separation and accumulation of Cu(II), Zn(II) and Cr(VI) from aqueous solution by magnetic chitosan modified with diethylenetriamine. Desalination 278, 397–404.


Prasanna, S. V. & Kamath, P. V. 2008 Chromate uptake characteristics of the pristine layered double hydroxides of Mg with Al. Solid State Sci. 10, 260–266.


First received 16 May 2012; accepted in revised form 26 November 2012