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Entrapment of Mg-Al layered double hydroxide in calcium alginate beads for phosphate removal from aqueous solution

Yong-Un Han[a], Won-Suk Lee[b], Chang-Gu Lee[a], Seong-Jik Park[c], Ki-Woo Kim[d], Song-Bae Kim[a]*

[a] *Department of Rural Systems Engineering and Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Korea*
Tel.: +8228804587; Fax: +8228732087; email: songbkim@snu.ac.kr
[b] *Department of Agricultural and Biological Engineering, University of Florida, Gainesville 32611, Florida, USA*
[c] *Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea*
[d] *School of Ecological and Environmental System, Kyungpook National University, Sangju 742-711, Korea*

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ABSTRACT

Mg-Al layered double hydroxide was entrapped in calcium alginate beads (LDH-alginate beads) for phosphate removal. A field emission scanning electron microscope (FESEM), combined with an energy dispersive X-ray spectrometer and an X-ray diffractometer, were used to analyze the properties of LDH-alginate beads. Batch and flow-through column experiments were performed to examine phosphate removal in LDH-alginate beads. FESEM images show that the cross-sectional surface of LDH-alginate beads was heterogeneous in surface topography, and LDH powders were intermingled with alginate polymers. Experimental results indicate that Mg-Al LDH-alginate beads are effective in the removal of phosphate. Batch experiments indicate that phosphate removal in 8% LDH-alginate beads was not sensitive to initial solution pHs between 4.9 and 8.9. Kinetic experiments demonstrate that phosphate removal reached equilibrium around 12 h of reaction time. Column experiments show that the removal capacity of 8% LDH-alginate beads was two orders of magnitude greater than that of pure alginate beads.

Keywords: Layered double hydroxides; Calcium alginate beads; Phosphate removal; Sorption; Batch experiment; Column experiment

1. Introduction

Layered double hydroxides (LDHs) are a class of nanostructured anionic clays. They have a general formula of $[\mathrm{M}1-x^{2+}\mathrm{M}x^{3+}(\mathrm{OH})2]^{x+}(\mathrm{A}^{n-})x/n\cdot m\mathrm{H2O}$, where M^{2+} is the divalent cation, M^{3+} is the trivalent cation, x is the molar ratio of $\mathrm{M}^{3+}/(\mathrm{M}^{2+}+\mathrm{M}^{3+})$, and A is the interlayer anion of valence n. LDHs consist of positively charged brucite-like sheets which are balanced by the intercalation of anions in the hydrated interlayer regions [1–4]. Because of the high surface area, large anion exchange capacity, and good thermal stability [5–7], LDHs have been studied for their potential application to the removal of oxyanions, such as arsenate/arsenite, chromate, selenate/selenite, borate, and nitrate from contaminated waters [7–19]. The removal of oxyanions by LDHs can be ascribed to three different mechanisms,

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*Corresponding author

including surface adsorption, interlayer anion exchange, and reformation effect [4,20–22].

The pollution of water bodies by phosphorus, an essential macronutrient, is a widespread environmental problem, causing eutrophication in lakes and seas and posing a great threat to aquatic environments. The use of LDHs to remove phosphate has been investigated by several researchers. They have examined the possibility of phosphate uptake by Mg-Al LDH [23,24], ion exchange between chloride and phosphate into zinc-aluminum (Zn-Al) LDH [25], phosphate removal by iron-based LDHs [26], and characterization of magnesium-manganese (Mg-Mn) LDH for the removal of phosphate from seawater [27]. They also investigated the comparison of various calcined LDHs on the phosphate removal [28], removal of phosphate in waste sludge filtrate using Zn-Al LDH [24], and enhancement of the phosphate removal capacity of Zn-Al LDH through the incorporation of zirconium [30]. These studies have shown that LDHs could be applicable to the removal of phosphate from aqueous solution.

However, the powdered form of LDH is not suitable in wastewater treatment/filtration systems because of its low hydraulic conductivity. As an alternative, granular LDHs could be used in fixed-bed filtration systems [4]. However, few studies have been performed so far using granular forms of LDHs to remove contaminants, including the removal of MS2 bacteriophage using Mg-Al LDH-coated sand [31], application of Mg-Al LDH aggregates to arsenic removal [13], carbon dioxide adsorption to Mg-Al LDH coated on zeolite [32], and phosphate removal with granular Mg-Al LDH as granular media [33]. Further experiments should be performed in order to improve our knowledge regarding phosphate removal using granular forms of LDHs.

Functional materials can be immobilized into calcium alginate beads for water treatments [34–36]. The entrapment using alginate beads is widely applied because it is a simple and cost effective technique. Sodium alginate is a nontoxic and biodegradable natural polymer, which is composed of (1-4)-linked D-mannuronic and L-glucuronic acid repeat units. Calcium ions can chelate carboxylate groups, make crosslinks between chains, and form an insoluble hydrogel [37]. The objective of this study was to synthesize the LDH-alginate beads through entrapping Mg-Al LDH into calcium alginate beads and to apply them for phosphate removal from aqueous solution. A field emission scanning electron microscope (FESEM) combined with an energy dispersive X-ray spectrometer (EDS) and an X-ray diffractometer (XRD) were used to analyze the properties of LDH-alginate beads. Batch and column experiments were performed to examine the removal of phosphate in LDH-alginate beads.

2. Materials and methods

2.1. Preparation of 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 Das et al. [28]. 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 alkali solution (pH = 13) of sodium hydroxide (NaOH) and sodium carbonate (Na2CO3) under 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 Mg-Al LDH used for the preparation of LDH-alginate beads was finally obtained via thermal treatment at 300°C for 24 h in an electric muffle furnace (C-FMA, Vision Lab, Seoul, Korea).

2.2. Preparation of LDH-alginate beads

LDH-alginate beads were prepared by entrapping a powdered form of Mg-Al LDH in a calcium alginate gel. Two grams of sodium alginate powder were added to 200 mL deionized water to prepare sodium alginate solution at room temperature. Then, the desired amount of LDH (within a range of 0–10% w/v) was added to 200 mL alginate solution under intensive stirring to obtain a homogeneous suspension. The suspension, contained in a plastic syringe (outlet diameter = 2 mm), was allowed to drop into a stirred reservoir containing 500 mL 0.3 M calcium chloride ($CaCl_2$) solution in order to form 4.15 ± 0.23 mm (number of beads = 90) spherical LDH-alginate beads. The beads were allowed to cure in the same $CaCl_2$ solution for 24 h under stirring and then were rinsed with deionized water to remove any excess Ca^{2+}. The beads containing X% (w/v) of LDH were designated as X% LDH-alginate beads.

2.3. Characterization of LDH-alginate beads

LDH-alginate beads were observed and examined with X-ray microanalysis, as described in the literature

[38]. Briefly, specimens were mounted on metal stubs using carbon tape and sputter-coated with platinum (approximately 20 nm in thickness). Specimens were examined with a field emission scanning electron microscope (FESEM) (Supra 55VP; Carl Zeiss, Oberkochen, Germany) at an accelerating voltage of 3 kV. In addition, the elemental composition was determined with energy-dispersive X-ray spectrometry (EDS) (XFlash 4000; Bruker AXS, Berlin, Germany), combined with an electron microscope at an accelerating voltage of 15 kV. X-rays were collected with a detector fixed at a take-off angle of 35°, and region analysis and mapping were performed on the specimens. In addition, the powdered form of LDH was characterized using powder X-ray diffractometry (XRD, D5005, Bruker AXS, Berlin, Germany) with Cu Kα radiation.

2.4. Kinetic and equilibrium batch experiments

Phosphate removal in LDH-alginate beads was observed by kinetic and equilibrium batch experiments. The desired phosphate solution was prepared by diluting the stock solution (1,000 mgP/L), which was made from potassium dihydrogen phosphate (KH2PO4). All batch experiments were performed at a solution pH of 4.9 (excluding the pH effect tests). The first batch experiments were conducted to examine the effect of LDH content in alginate beads on phosphate removal. Two grams of LDH-alginate beads (0%, 2%, 4%, 6%, 8%, and 10%) were added to 30 mL phosphate solution (25 mgP/L) in 50 ml polypropylene conical tubes. The tubes were shaken at 25° and 40 rpm using a culture tube rotator (MG-150D, Mega Science, Seoul, Korea). The samples were collected 24 h post-reaction, and filtered through a 0.45-µm membrane filter. The phosphate was analyzed by the ascorbic acid method [39]. Phosphate concentrations were measured at a wavelength of 880 nm using a UV–vis spectrophotometer (Helios, Thermo Scientific, Waltham, MA, USA).

Further batch experiments were performed to observe the effect of solution pH on phosphate removal. The experiments were conducted at an initial phosphate concentration of 25 mgP/L with 2 g of 8% LDH-alginate beads. The initial solution pHs ranged from 4.9 to 8.9. The pH was measured with a pH probe (9107BN, Thermo Scientific, Waltham, MA, USA). Next, kinetic batch experiments were performed with 8% LDH-alginate beads at the initial phosphate concentrations of 15 and 25 mgP/L. The same procedure used for the first experiments was followed. In the experiments, the samples were taken at 1, 2, 3, 4, 5, 6, 12, and 24 h post-reaction. Equilibrium batch experiments were conducted with 8% LDH-alginate beads (2 g) at eight different initial phosphate concentrations. Samples were collected 12 h post-reaction, and all experiments were performed in triplicate.

2.5. Column experiments

Column experiments were performed using a Plexiglas column (inner diameter = 2.5 cm; bed depth = 20 cm; bulk volume = 98.2 cm^3) packed with 0% (mass of filter media = 71.6 g) and 8% LDH-alginate beads (mass of filter media = 92.2 g). Prior to the experiments, the packed column was flushed upward using a HPLC pump (Series II pump, Scientific Systems Inc., State College, PA, USA) operating at a rate of 0.5 ml min^{-1} with 5 bed volumes (BV; 1 BV = 27.0 cm^3) of deionized water until a steady state flow condition was established. Then, phosphate solution (10 mgP/L) was introduced to the packed column at the same flow rate. The experiments were performed at a pH of 4.9. Portions of the effluent were collected using the auto collector (Retriever 500, Teledyne, City of Industry, CA, USA) at a regular interval, and phosphate was analyzed by the ascorbic acid method [39].

2.6. Data analysis

The kinetic data can be analyzed using the following pseudo first-order and pseudo second-order models [40,41]:

$$q_t = q_e[1 - \exp(-k_1 t)], \tag{1}$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t, \tag{2}$$

where q_t is the amount of phosphate removed at time t (mgP/g), q_e is the amount of phosphate removed at equilibrium (mgP/g), k_1 is the pseudo-first-order rate constant (1/h), and k_2 is the pseudo-second-order velocity constant (g/mgP/h). The equilibrium data can be analyzed using the following Langmuir and Freundlich isotherm models:

$$q_e = \frac{Q_{\mathrm{m}} K_{\mathrm{L}} C}{1 + K_{\mathrm{L}} C}, \tag{3}$$

$$q_e = K_{\mathrm{F}} C^n, \tag{4}$$

where C is the concentration of phosphate in the aqueous solution at equilibrium (mgP/L), K_{L} is the Langmuir constant related to the binding energy (L/mgP), Q_{m} is the maximum mass of phosphate removed per unit mass of LDH-alginate beads (removal capacity) (mgP/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.

In the column experiments, the empty bed contact time (EBCT, min) can be determined as follows [42]:

$$\mathrm{EBCT} = \frac{V_r}{Q}, \tag{5}$$

where V_r is the fixed-bed volume (cm^3), and Q is the volumetric flow rate (mL/min). The total mass of phosphate injected into a column (M_{total}, mgP) during the experiment can be calculated as follows:

$$M_{\mathrm{total}} = \frac{C_0 Q t_{total}}{1000} \tag{6}$$

where C_0 is the influent concentration of phosphate (mgP/L), and t_{total} is the total flow time (min). The column capacity for phosphate removal at a given flow rate and influent concentration of phosphate (C_{cap}, mgP) can be quantified, as follows:

$$C_{\mathrm{cap}} = \frac{Q}{1000} \int_{t=0}^{t=t_{\mathrm{total}}} (C_0 - C)\,\mathrm{d}t, \tag{7}$$

where C is the effluent concentration of phosphate (mgP/L). The total percent of phosphate removed during the experiment (R, %) can be calculated, as follows:

$$R = \left(\frac{C_{\mathrm{cap}}}{M_{\mathrm{total}}}\right) \times 100. \tag{8}$$

The mass of phosphate removed per unit mass of LDH-alginate beads in the column (removal capacity of LDH-alginate beads q_{a}, mgP/g) can be determined, as follows:

$$q_{\mathrm{a}} = \frac{C_{\mathrm{cap}}}{M_{\mathrm{f}}}, \tag{9}$$

where M_{f} is the mass of LDH-alginate beads in the column (g).

3. Results and discussion

3.1. Characteristics of LDH-alginate beads

FESEM images and XRD patterns for the powdered form of LDH are presented in Fig. 1. Our XRD pattern was similar to the XRD data for Mg-Al LDH provided in the literature with sharp and intense line at low 2θ and less intense lines at high 2θ [23,24,31]. The synthesized Mg-Al LDH had a chemical composition of $Al_8O_3N_6{+}Al_{0.56}Mg_{0.44}$. FESEM showed the cross-sectional surface of pure alginate beads (Fig. 2a). The surface appeared to be homogeneous overall in surface topography. Calcium was evident at the peak positions of 3.69 and 4.01 keV as K alpha and K beta X-ray signals, respectively (Fig. 2b). Chloride was also detected at the peak position of 2.62 keV as K alpha X-ray signal. Meanwhile, the cross-sectional surface of LDH-alginate beads was rather heterogeneous in surface topography (Fig. 2c). In addition to calcium and chloride, magnesium and aluminum were found at 1.25 and 1.48 keV as K alpha X-ray signals, respectively (Fig. 2d). It was common to observe powders of LDH intermingled with calcium alginate polymers at a higher magnification (Fig. 2e). Instances were also noted where sheet-like polymer matrices were present on the cross-sectional surface of LDH-alginate beads (Fig. 2f).

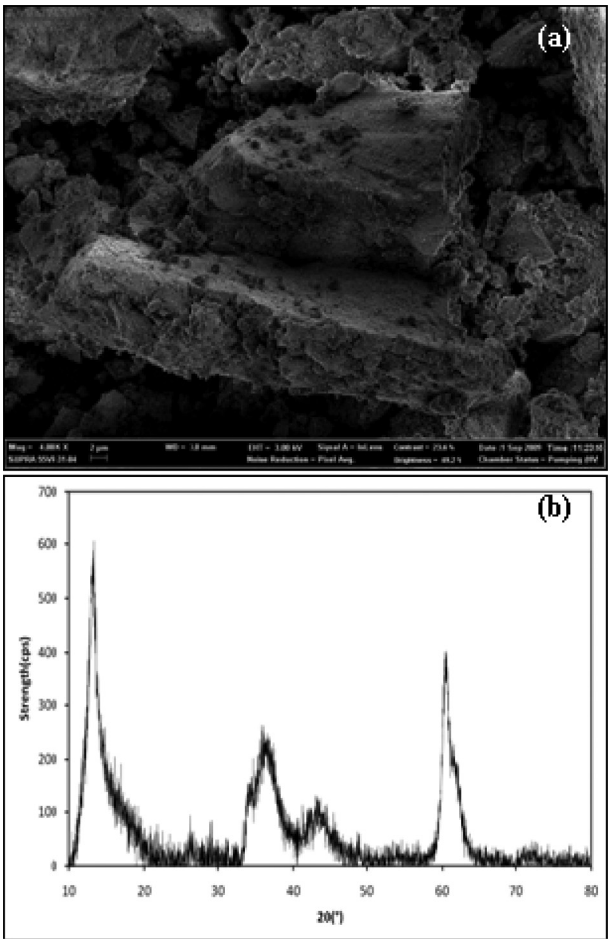

Fig. 1. A powdered form of layered double hydroxides: (a) field emission scanning electron micrograph (bar = 2 μm); (b) X-ray diffraction pattern.

The spatial distribution of specific elements was revealed through EDS mapping analysis. The secondary electron image of LDH-alginate beads (Fig. 3a) was overlaid with magnesium map (Fig. 3c) and aluminum

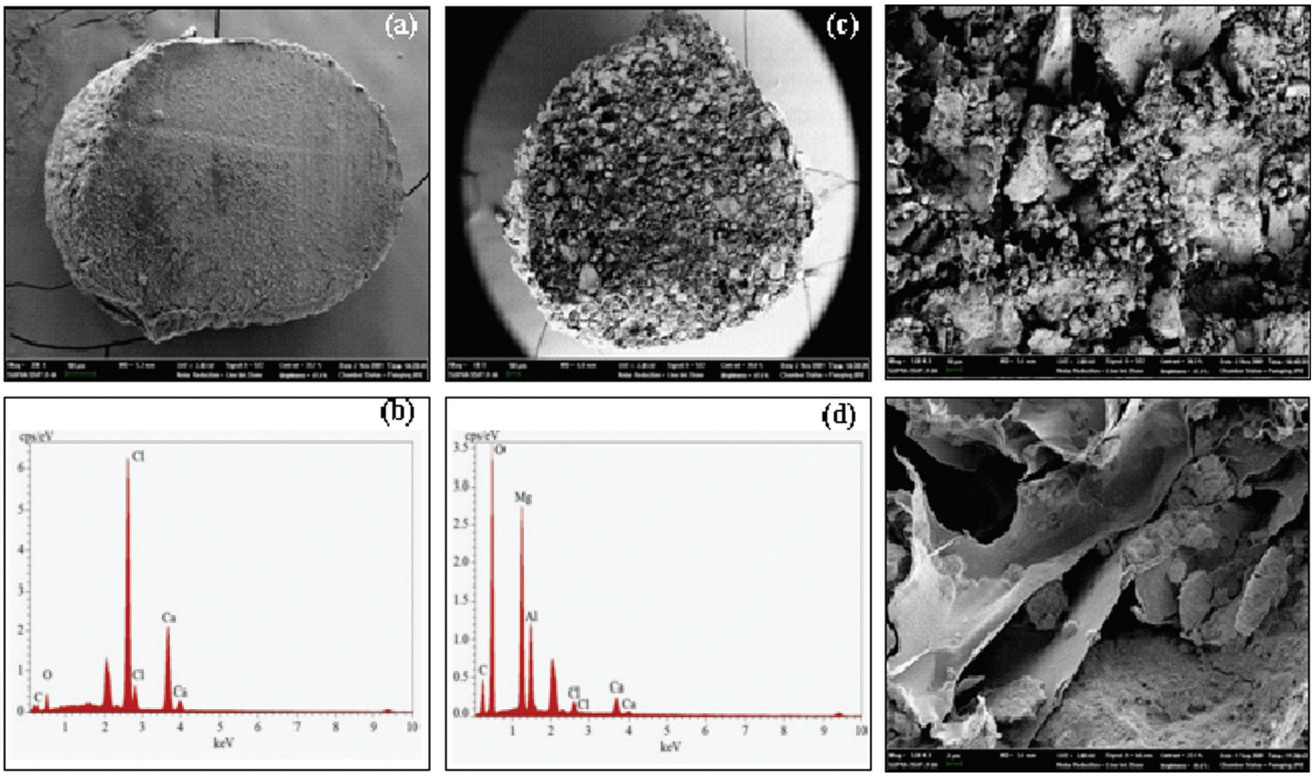

Fig. 2. Field emission scanning electron micrographs (FESEM) of layered double hydroxide-loaded alginate beads (LDH-alginate beads): (a) cross-sectional view of pure alginate beads (0% LDH-alginate beads) (bar = 100 μm); (b) X-ray spectrum (EDS) of pure alginate beads; (c) cross-sectional view of 8% LDH-alginate beads (bar = 100 μm); (d) X-ray spectrum (EDS) of 8% LDH-alginate beads; (e) FESEM image of 8% LDH-alginate beads (bar = 10 μm); (f) FESEM image of 8% LDH-alginate beads (bar = 2 μm).

map (Fig. 3d). It is shown that magnesium and aluminum appeared to be prevalent throughout the surface, despite the topographical relief and detector position (Fig. 3b). Each element map (Fig. 3c and 3d) demonstrated that the two elements were localized on almost the same regions on the cross-sectional surface of LDH-alginate beads.

3.2. *Effects of LDH content and solution pH on phosphate removal*

The effect of the LDH content in alginate beads on the phosphate removal is shown in Fig. 4. For the experiments where no LDH was added to alginate beads (0%), the average removal was 14.1%. At an LDH content of 2%, the average removal was 86.4%, indicating a sharp increase in phosphate removal in the presence of LDH. When the content increased from 2% to 4%, average removal increased 9.1% (from 86.4% to 95.5%). Another 2% increase in LDH content from 4% to 6% resulted in a 0.6% incremental increase in phosphate removal (from 95.5% to 96.1%). The increase in removal was 2.5% (from 96.1% to 98.6%) when the LDH content was increased from 6% to 8%. Finally, 99.1% of phosphate was removed with 10% LDH content. Fig. 4 shows a rapid increase in removal between 0% and 4%, followed by a leveling out between 4% and 10%. This indicates that removal efficacy is not linearly dependent on LDH content in given experimental conditions. For further experiments, 8% LDH-alginate beads were used because a higher percentage (10%) was found to cause clogging at the outlet of the plastic syringe during the synthesis of LDH-alginate beads.

Our results indicate that Mg-Al LDH-alginate beads (molar ratio = 2:1) are effective in the removal of phosphate. According to Das et al. [28] who have performed the phosphate removal experiments using the powdered form of LDHs with varying $M^{2+}-M^{3+}$ cations, Mg-Al LDH was the most effective in phosphate removal from a KH_2PO_4 solution of eight different LDHs. The authors demonstrated that, among three Mg-Al LDHs with molar ratios of 2:1, 3:1 and 4:1, the 2:1 LDH was the best at phosphate removal. Cheng et al. [29] have reported, however, that Zn-Al LDH was the best of ten different LDHs (better than Mg-Al LDH) at the removal of phosphate from sewage sludge

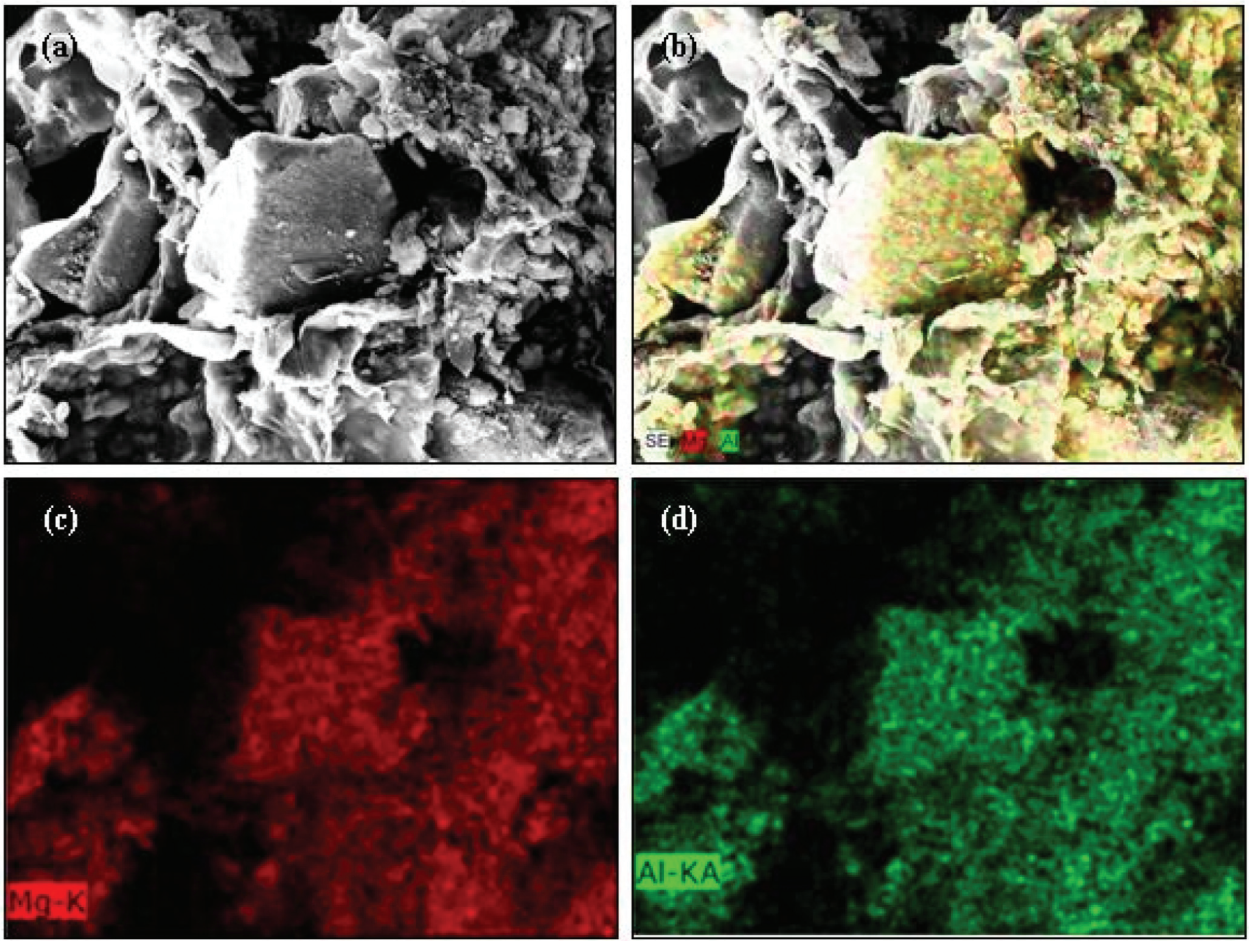

Fig. 3. Field emission scanning electron micrographs of layered double hydroxide-loaded alginate beads: (a) 8% LDH-alginate beads; (b) overlay of the secondary electron image, aluminum map, and magnesium map; (c) magnesium map; (d) aluminum map.

filtrate. They have shown that 2:1 Zn-Al LDH was the best of five Mg-Al LDHs with different molar ratios. In addition, Chitrakar et al. [27] have demonstrated that Mg-Mn LDH was far better than Mg-Al LDH at phosphate uptake from phosphate-enriched seawater. This discrepancy may be ascribed to different conditions used in the synthesis of LDH (aging conditions, calcination temperature, etc.) and removal experiments (solution composition, solution pH, etc.).

The effect of initial pH on phosphate removal in 8% LDH-alginate beads is presented in Fig. 5. The average removal efficacy at a pH of 4.9 was 98.6% and decreased slightly to 95.5% as the solution pH approached 8.9, indicating that phosphate removal in Mg-Al LDH-alginate beads was not sensitive to solution pH changes between 5.0 and 9.0 under given experimental conditions. Our results are not consistent with the report of Das et al. [28], who have examined the influence of solution pH on phosphate removal for the powdered form of Mg-Al LDH. They demonstrated a decreasing tendency in phosphate removal (a sharp decrease from 91.7% to 39.0%) with pH increasing from

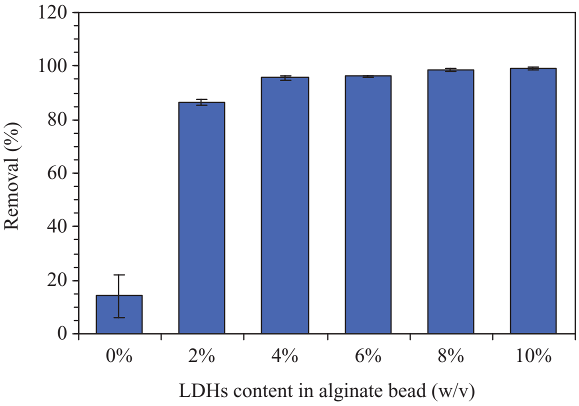

Fig. 4. Effect of layered double hydroxides (LDHs) content in alginate beads on phosphate removal (initial phosphate concentration = 25 mgP/L; solution pH = 4.9).

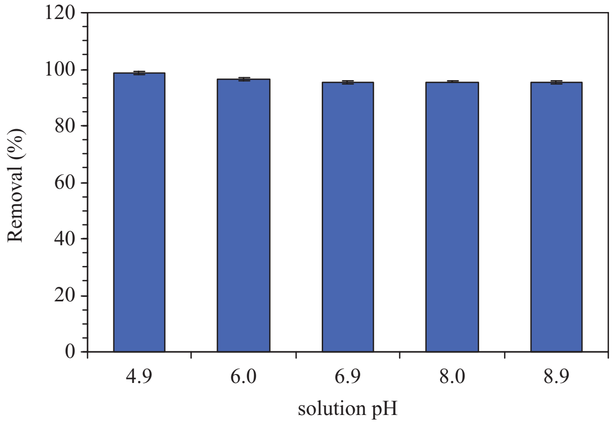

Fig. 5. Effect of solution pH on phosphate removal in 8% LDH-alginate beads (initial phosphate concentration = 25 mgP/L).

5.0 to 10.0. Other experiment has investigated the effect of pH on phosphate removal in Mg-Al LDH [23]. The experiment showed an increase in phosphate uptake with pH increase from 5.5 to 7.0 but a decrease between 7.0 and 9.5.

3.3. Phosphate removal kinetics and isotherms

The removal kinetics of phosphate in 8% LDH-alginate beads is shown in Fig. 6. The removal reached equilibrium around 12 h of reaction time. Model parameters for the pseudo-first-order and pseudo second-order models obtained from the kinetic experiments are provided in Table 1. In the pseudo-first-order model, the value of q_e at 15 mgP/L was 0.202 mgP/g. At 25 mgP/L, it was 0.356 mgP/g, which is about 1.8 times greater than that at 15 mgP/L. The value of k_1 at 15 mgP/L was 1.185 1/h while it was 1.214 1/h at 25 mgP/L, indicating that the reaction rate at 25 mgP/L was faster than that at 15 mgP/L. The values of q_e from the pseudo-second-order model were similar to those from the pseudo-first-order model. At 15 mgP/L, the value of q_e was 0.216 mgP/g, while it was 0.381 mgP/g at 25 mgP/L. The values of k_2 at 15 and 25 mgP/L were 10.065 and 5.945 g/mgP/h, respectively, indicating that the velocity constant at 15 mgP/L was about 1.7 times greater than that at 25 mgP/L. The correlation coefficients (R^2) indicated that the pseudo-second-order model described the kinetic data better than the pseudo first-order model.

Table 1
Model parameters for the pseudo first-order and pseudo second-order models obtained from the kinetic batch experiments in 8% LDH-alginate beads

Initial phosphate concentration (mgP/L)	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mgP/g)	k_1 (1/h)	R^2	q_e (mgP/g)	k_2 (1/h)	R^2
15	0.202	1.185	0.908	0.216	10.065	0.995
25	0.356	1.214	0.900	0.381	5.945	0.995

The equilibrium isotherms of phosphate on 8% LDH-alginate beads are presented in Fig. 7. In the Freundlich model, the distribution coefficient (K_F) was 0.516 L/g, while the Freundlich constant (n) was 0.384. In the Langmuir model, the Langmuir constant (K_L) was 2.018 L/mgP, while the removal capacity (Q_m) was 1.039 mgP/g. The correlation coefficient (R^2) of the Freundlich model (=0.951) was greater than that of the Langmuir model (=0.848), indicating that the Freundlich isotherm was appropriate at describing the experimental result.

In our experiments, phosphate ions in aqueous solution could diffuse into calcium alginate beads through the pores in the beads. Then, phosphate ions

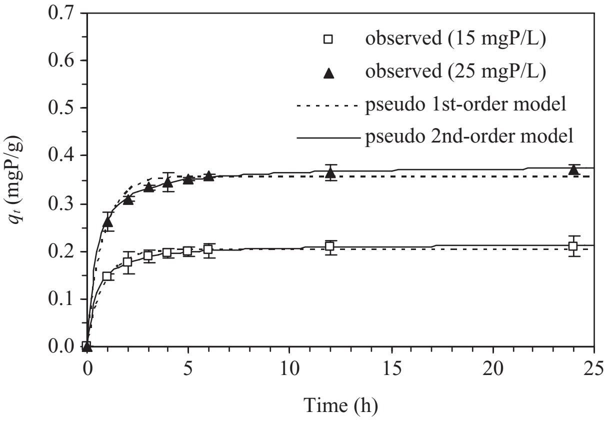

Fig. 6. Kinetic batch data and model fit for phosphate removal in 8% LDH-alginate beads.

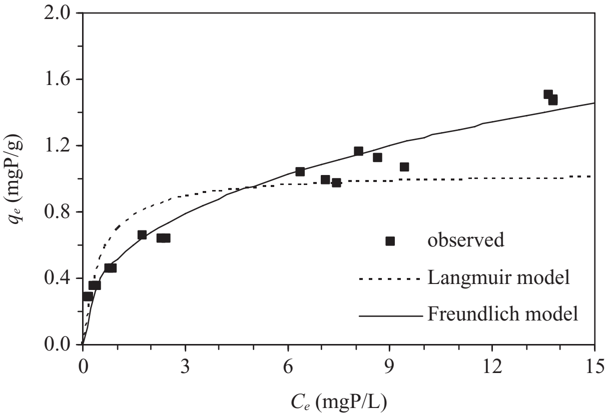

Fig. 7. Equilibrium batch data and model fit for phosphate removal in 8% LDH-alginate beads.

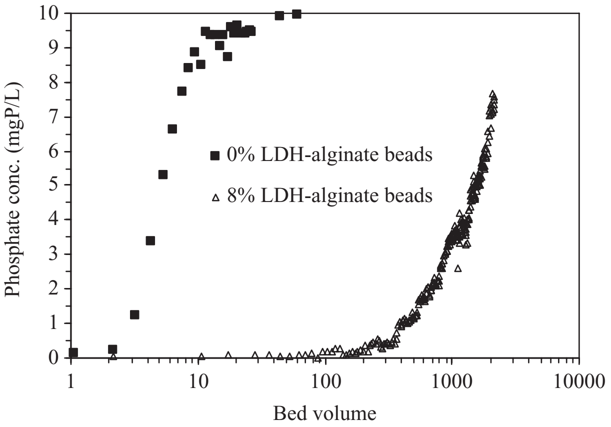

Fig. 8. Breakthrough curves for phosphate removal in 8% LDH-alginate beads (1 bed volume = 27.0 cm^3).

could come in contact with the entrapped Mg-Al LDH particles and subsequently be removed from aqueous phase to solid phase (LDH). Three different mechanisms might be involved in the removal of phosphate to LDH. In surface adsorption, the negatively-charged phosphate could adsorb to the positively-charged brucite-like layer. Also, phosphate could replace the charge balancing anion (carbonate) in the interlayer region via anion exchange process. Furthermore, phosphate could intercalate into the interlayer during the reconstruction/rehydration of the calcined LDH in an aqueous medium (reformation effect) [4,29,30].

3.4. Phosphate removal in flow-through columns

The breakthrough curves (BTCs) for phosphate removal in 0% (pure alginate beads) and 8% LDH-alginate beads are presented in Fig. 8. The breakthrough data are presented in terms of phosphate concentration versus BV. At the given conditions (C_0 = 10 mgP/L, Q = 0.5 mL/min) in 0% LDH-alginate beads, the BTC increased sharply, reaching 95% of the initial phosphate concentration (=9.5 mgP/L) around 13 BV. Under the same experimental conditions, the BTC for 8% LDH-alginate beads was distinctively delayed relative to the BTC for 0% LDH-alginate beads. In 8% LDH-alginate beads, no breakthrough appeared around 50 BV, and then the BTC increased slowly, reaching C = 1 mgP/L around 150 BV. Thereafter, the BTC increased continuously, arriving at C = 9.5 mgP/L around 1020 BV.

The column experimental results in 0% (pure alginate beads) and 8% LDH-alginate beads are provided in Table 2. In 0% LDH-alginate beads, the column capacity for phosphate removal (C_{cap}) was 1.1 mgP, while it was 143.6 mg in 8% LDH-alginate beads, which is about 130 times higher than that of 0% LDH-alginate beads. The total removal efficacy (R) of 0% and 8% LDH-alginate beads was 26.0% and 51.9%, respectively. The removal capacity (q_a) was 0.016 mgP/g in 0% LDH-alginate beads, while it was 1.558 mgP/g in 8% LDH-alginate beads (=1.558 mgP per one gram of beads). In the separate batch experiments, the removal capacity of our Mg-Al LDH powder was determined to be 37.4 mgP per one gram of powders, which was in the ranges of the removal capacity for Mg-Al LDH powders (=7.3–81.6 mgP/g) reported in the literature [4].

4. Conclusions

In this study, Mg-Al LDH was entrapped in calcium alginate beads for phosphate removal. Image analyses show that LDH powders were intermingled with alginate polymers. Batch experiments indicate that the 8% LDH-alginate beads are effective in the removal of phosphate. Column experiments show that the phosphate removal capacity of 8% LDH-alginate beads was two orders of magnitude greater than that of pure alginate beads. This study demonstrates the potential use of LDH-alginate beads for phosphate removal in flow-through filtration systems. However, further experiments are required to examine the stability of LDH-alginate beads in various solution conditions.

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Table 2
Column experimental results for phosphate removal in 0% (pure alginate beads) and 8% LDH-alginate beads

Filter media	C_0 (mgP/L)	Q (mL/min)	EBCT (min)	M_{total} (mgP)	C_{cap} (mgP)	R (%)	q_a (mgP/g)	M_f (g)
0% LDH-alginate beads	10	0.5	54.0	4.4	1.1	26.0	0.016	71.6
8% LDH-alginate beads	10	0.5	54.0	277.0	143.6	51.9	1.558	92.2

References

[1] S.J. Palmer and R.L. Frost, Effect of pH on the uptake of arsenate and vanadate by hydrotalcites in alkaline solutions: a Raman spectroscopic study, J. Raman Spectrosc., 42 (2011) 224–229.

[2] S.J. Palmer and R.L. Frost, Use of hydrotalcites for the removal of toxic anions from aqueous solutions, Ind. Eng. Chem. Res., 49 (2010) 8969–8976.

[3] S.J. Palmer, R.L. Frost and H.J. Spratt, Synthesis and Raman spectroscopic study of Mg/Al,Fe hydrotalcites with variable cationic ratios, J. Raman Spectrosc., 40 (2009) 1138–1143.

[4] K.H. Goh, T.T. Lim and Z. Dong, Application of layered double hydroxides for removal of oxyanions: A review, Water Res., 42 (2008) 1343–1368.

[5] F. Cavani, F. Trifirb and A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today, 11 (1991) 173–301.

[6] A. Vaccari, Preparation and catalytic properties of cationic and anionic clays, Catal. Today, 41 (1998) 53–71.

[7] N.N. Das, J. Konar, M.K. Mohanta and S.C. Srivastava, Adsorption of Cr(VI) and Se(IV) from their aqueous solutions onto Zr4+−substituted ZnAl/MgAl-layered double hydroxides: effect of Zr4+ substitution in the layer, J. Colloid Interf. Sci., 270 (2004) 1–8.

[8] R.L. Goswamee, P. Sengupta, K.G. Bhattacharyya and D.K. Dutta, Adsorption of Cr(VI) in layered double hydroxides, Appl. Clay Sci., 13 (1998) 21–34.

[9] Y. You, G.F. Vance and H. Zhao, Selenium adsorption on Mg–Al and Zn–Al layered double hydroxides, Appl. Clay Sci., 20 (2001) 13–25.

[10] M. del Arco, S. Gutierrez, C. Martin, V. Rives and J. Rocha, Effect of the Mg:Al ratio on borate(or silicate)/nitrate exchange in hydrotalcite, J. Solid State Chem., 151 (2000) 272–280.

[11] S. Tezuka, R. Chitrakar, A. Sonoda, K. Ooi and T. Tomida, Studies on selective adsorbents for oxy-anions: Nitrate ion-exchange properties of layered double hydroxides with different metal atoms, Green Chem., 6 (2004) 104–109.

[12] N.K. Lazaridis, T.A. Pandi and K.A. Matis, Chromium(VI) removal from aqueous solutions by Mg-Al-CO3 hydrotalcites: Sorption-desorption kinetic and equilibrium studies, Ind. Eng. Chem. Res., 43 (2004) 2209–2215.

[13] G.P. Gillman, A simple technology for arsenic removal from drinking water using hydrotalcite, Sci. Total Environ., 336 (2006) 926–931.

[14] R.L. Frost and A.W. Musumeci, Nitrate adsorption through hydrotalcite reformation, J. Colloid Interf. Sci., 302 (2006) 203–206.

[15] S.L. Wang, R.J. Hseu, R.R. Chang, P.N. Chiang, J.H. Chen and Y.M. Tzou, Adsorption and thermal desorption of Cr(VI) on Li/Al layered double hydroxide, Colloid Surf. A., 277 (2006) 8–14.

[16] S.L. Wang, C.H. Liu, M.K. Wang, Y.H. Chuang and P.N. Chiang, Arsenate adsorption by Mg/Al–NO3 layered double hydroxides with varying the Mg/Al ratio, Appl. Clay Sci., 43 (2009) 79–85.

[17] A. Violante, M. Pucci, V. Cozzolino, J. Zhu and M. Pigna, Sorption/desorption of arsenate on/from Mg–Al layered double hydroxides: Influence of phosphate, J. Colloid Interf. Sci., 333 (2009) 63–70.

[18] R. Liu, R.L. Frost and W.N. Martens, Absorption of the selenite anion from aqueous solutions by thermally activated layered double hydroxide, Water Res., 43 (2009) 1323–1329.

[19] M. Islam and R. Patel, Nitrate sorption by thermally activated Mg/Al chloride hydrotalcite-like compound, J. Hazard. Mater., 169 (2009) 524–531.

[20] F. Li and X. Duan, Applications of layered double hydroxides, Struct. Bond., 119 (2005) 193–223.

[21] R.L. Frost, A.W. Musumeci, M.O. Adebajo and W. Martens, Using thermally activated hydrotalcite for the uptake of phosphate from aqueous media, J. Thermal Anal. Calorim., 89 (2007) 95–99.

[22] R.L. Frost, A.W. Musumeci, J.T. Kloprogge, M.O. Adebajo and W.N. Martens, Raman spectroscopy of hydrotalcites with phosphate in the interlayer: implications for the removal of phosphate from water, J. Raman Spectrosc., 37 (2006) 733–741.

[23] A. Ookubo, K. Ooi and H. Hayashi, Preparation and phosphate ion-exchange properties of a Hydrotalcite-like compound, Langmuir, 9 (1993) 1418–1422.

[24] H.S. Shin, M.J. Kim, S.Y. Nam and H.C. Moon, Phosphorus removal by hydrotalcite-like compounds (HTLcs), Water Sci. Technol., 34 (1996) 161–168.

[25] M. Badreddine, A. Legrouri, A. Barroug, A. De Roy and J.P. Besse, Ion exchange of different phosphate ions into the zinc-aluminum-chloride layered double hydroxide, Mater. Lett., 38 (1999) 391–395.

[26] Y. Seida and Y. Nakano, Removal of phosphate by layered double hydroxides containing iron, Water Res., 36 (2002) 1306–1312.

[27] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, K. Ooi and T. Hirotsu, Adsorption of phosphate from seawater on calcined MgMn-layered double hydroxides, J. Colloid Interf. Sci., 290 (2005) 45–51.

[28] J. Das, B.S. Patra, N. Baliarsingh and K.M. Parida, Adsorption of phosphate by layered double hydroxides in aqueous solutions, Appl. Clay Sci., 32 (2006) 252–260.

[29] X. Cheng, X. Huang, X. Wang, B. Zhao, A. Chen and D. Sun, Phosphate adsorption from sewage sludge filtrate using zinc–aluminum layered double hydroxides, J. Hazard. Mater., 169 (2009) 958–964.

[30] P. Koilraj and S. Kannan, Phosphate uptake behavior of ZnAlZr ternary layered double hydroxides through surface precipitation, J. Colloid Interf. Sci., 341 (2009) 289–297.

[31] Y .You, G.F. Vance, D.L. Sparks, J. Zhuang and Y. Jin, Sorption of MS2 bacteriophage to layered double hydroxides: Effects of reaction time, pH, and competing anions, J. Environ. Qual., 32 (2003) 2046–2053.

[32] M.R. Othman, N.M. Rasid and W.J.N. Fernando, Mg-Al hydrotalcite coating on zeolites for improved carbon dioxide adsorption, Chem. Eng. Sci., 61 (2006) 1555–1560.

[33] K. Kuzawa, Y.J. Jung, Y. Kiso, T. Yamada, M. Nagai and T.G. Lee, Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent, Chemosphere, 62 (2006) 45–52.

[34] M.Y. Arıca, G. Bayramoğlu, M, Yilmaz, S. Bektaş and Ö. Genç, Biosorption of Hg^{2+}, Cd^{2+}, and Zn^{2+} by Ca-alginate and immobilized wood-rotting fungus *Funalia trogii*, J Hazard. Mater., B109 (2004) 191–199.

[35] C. Escudero, N. Fiol, I. Villaescusa and J.-C. Bollinger, Arsenic removal by a waste metal (hydr)oxide entrapped into calcium alginate beads, J. Hazard. Mater., 164 (2009) 533–541.

[36] A.N. Bezbaruah, S. Krajangpan, B.J. Chisholm, E. Khan and J.J.E. Bermudez, Entrapment of iron nanoparticle in calcium alginate beads for groundwater remediation applications, J. Hazard. Mater., 166 (2009) 1339–1343.

[37] M. Kobašlija and D.T. McQuade, Removable colored coatings based on calcium alginate hydrogels, Biomacromolecules, 7 (2006) 2357–2361.

[38] C.H. Yoon and K.W. Kim, Anatomical descriptions of silicified woods from Madagascar and Indonesia by scanning electron microscopy, Micron, 39 (2008) 825–831.

[39] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater. Washington, DC, 1995.

[40] Y.S. Ho and G. Mckay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[41] T. Mathialagan and T. Viraraghavan, Adsorption of cadmium from aqueous solutions by vermiculite, Sep. Sci. Technol., 38 (2003) 57–76.

[42] H.C. Kim, S.J. Park, C.G. Lee, Y.U. Han, J.A. Park and S.B. Kim, Humic acid removal from water by iron-coated sand: A column experiment, Environ. Eng. Sci., 14 (2009) 41–47.