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Preparation and evaluation of layered double hydroxides (LDHs) for phosphate removal

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ABSTRACT

Nitrate-intercalated layered double hydroxides (LDHs) were prepared and assessed for phosphate removal from water. The sorption experiments for phosphate uptake were carried out as a function of LDHs' dose, contact time, initial pH of solution and initial phosphate concentration. The results show that about 97–99% phosphate removal was achieved at dose 0.3 g/L for the 10 mg-P/L test solution by Ca-based LDHs. The adsorption data fitted well with Langmuir isotherm and the maximum sorption capacity can be up to 70.9 mg-P/g of adsorbent. All selected Ca-based LDHs were observed to have a strong buffering capacity, indicating the suitability of potential application under different pH systems. The results also demonstrated that the real effluent from a wastewater treatment plant with high P content (3.4–10.4 mg/L) can be treated by Ca–Al-60 LDH with more than 90% P removal.

Keywords: Adsorption; Layered double hydroxide (LDH); Ca-based LDH; Phosphate removal

1. Introduction

The presence of excess phosphate in the domestic sewage and industrial effluents discharged to natural water has long been viewed as the cause of algae blooms and eutrophication. The average molar ratio of nitrogen, phosphorus and carbon in algae protoplasm is approximately 15:1:105 [1] and if any of these components is less than this ratio, it will limit the algae growth. In general, a minimal amount of phosphorus can cause substantial algae growth and its removal is more crucial in comparison with nitrogen removal for preventing algae glooming and eutrophication.

The typical phosphate concentration in crude sewage ranges between 5 and 30 mg/L [2]. European Union (EU) legislation makes phosphate removal from sewage compulsory. The EU Urban Waste Water Treatment Directive [3] introduced requirements for the control of phosphorus (P) and nitrogen (N) concentrations in the effluent, which was taken into force in England and Wales [4] and Scotland [5] in November 1994, whereby a significant reduction of P and N was required if the effluent is to be discharged in a given area that is sensitive to eutrophication. Total P concentration should not exceed 2 mg/L in the final

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effluent in an area with a population equivalent (p.e.) to a range between 10,000 and 100,000 and not exceed to 1 mg/L when the p.e. is greater than 100,000.

The major treatment processes to remove and recover phosphate from wastewaters include ion exchange, chemical precipitation, biological treatment, crystallisation and adsorption [6–10]. Although chemical precipitation and biological removal of phosphate have been used widely in industry, both of these require high operational cost. Moreover, chemical precipitation causes problem for sludge handling and its disposal due to chemical treatment. On the other hand, biological treatment is a slow and complex operation process and unsuitable for treating wastewater containing high concentration of phosphate [8]. Besides, the recovery and reuse of phosphorus is an attractive research topic now-a-days for the sustainable environment of the world, because it is a non-renewable natural resource and it is estimated to be depleted by 2050 [9]. Thus, the adsorptive removal of phosphate became appealing due to its flexibility and simplicity of design, ease of operation, low cost and the possibility of phosphate recovery. Various low-cost adsorbents have been studied for phosphate removal such as fly ash, blast furnace slag, zeolite, iron oxides, red mud, aluminium salts, etc. However, the maximum phosphorus adsorption capacity of many of such sorbent materials was not satisfactory and hence, these were not used widely [9,11]. So, the research in the recent years has focused on developing efficient adsorbents with high sorption capacity, and layered double hydroxides (LDHs) have been identified and proposed as a good ion exchangers and adsorbents [12].

LDHs, also known as hydrotalcite-like compounds (HTlcs) are a class of two-dimensional nanostructured anionic clays. The general formula of LDH structures can be represented as $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} denote divalent (e.g. Mg^{2+}, Zn^{2+}, Ca^{2+}, etc.) and trivalent cations (e.g. Al^{3+}, Fe^{3+}, Cr^{3+}, etc.), respectively; A^{n-} is the interlayer anion of valence n, such as NO_3^-, SO_4^{2-}, CO_3^{2-}, etc. and x is equal to the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$ typically ranges from 0.18 to 0.33 [12–14]. These materials consist of positively charged, brucite-like octahedral layers and a negatively charged interlayer region containing anions and water molecules. The positive charges generated from the isomorphous substitution of trivalent cations for divalent cations are balanced by interlayer anions that can be exchanged for other anions, giving LDHs a good anion-exchange property. In recent years, a number of studies have reported phosphate removal by different isostructural LDH compounds that were prepared with a great diversity in metal precursors (i.e. cation pairs), intercalated anions and synthesis methods [15]. In general, the most selected divalent and trivalent cations were Mg^{2+}, Ca^{2+} and Al^{3+}, Fe^{3+}, respectively, with CO_3^{2-} and Cl^- as the frequently used intercalated anions [16]. Very few studies prepared LDH with NO_3^- as the intercalated anion, though this monovalent ion in the interlayer space of the LDHs can be readily exchanged with other anions [17]. In fact, LDHs have the affinity for monovalent inorganic anions in the order of $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, and generally have greater affinity for multivalent inorganic anions (e.g. CO_3^{2-}) compared with monovalent inorganic anions [18,19]. This was also in correspondence to the higher sorption capacity of Mg–Al–LDH(X) in the order of X: $NO_3^- > Cl^- > CO_3^{2-}$ [20].

In the present study, a number of NO_3^--intercalated LDHs were prepared in order to study the performance of these LDHs to remove phosphate from aqueous solution as well as from real effluents of wastewater treatment plant and thereby, to identify the best metal precursors for phosphate-specific LDH sorbents. The sorption experiments for phosphate uptake were carried out as a function of LDHs' dose, contact time, initial pH of solution and initial adsorbate concentration.

2. Materials and experimental procedures

2.1. Synthesis of LDH compounds

Based on the combination of divalent (M^{II}: Mg^{2+}, Ca^{2+}) and trivalent (M^{III}: Al^{3+}, Fe^{3+}) cations such as Mg–Al, Ca–Al, Mg–Fe, Ca–Fe, MgCa–Al and MgCa–Fe, and two drying temperatures (60 and 450℃), a total of 20 different LDHs were prepared by the coprecipitation method, following a method described by Jiang et al. [13]. In this method, one solution (150 mL) containing 0.2 mol of M^{II} and 0.1 mol of M^{III} nitrate salts (corresponding to a M^{II}/M^{III} molar ratio = 2) was slowly added to a second solution containing 2.0 M NaOH (300 mL) by a peristaltic pump for about 130–150 min and under vigorous mechanical stirring by Flocculator (SW6, Stuart) at 250 rpm. During this process, the pH was 12.6–13.5 and the reaction was always performed at room temperature. After mixing, the thick slurry was aged at 85℃ for 2 h, and the pH after ageing was around 10–11 for most of the samples, except the samples with Mg–Al and Mg–Fe (the corresponding pH were 8 and 8.6, respectively). The solid precipitates were separated by centrifugation at a speed of 1,500 rpm for 25 min, which then filtered (using Whatman Grade 6 filter paper) and washed four times with deionized water, and subsequently dried at 60℃ for 24 h and 450℃ for 2 h, respectively. Finally, the

dried LDH compounds were crushed to powders and stored in screw-top 22 mL glass vial kits with the level as Ca–Al-60, Ca–Al-450, Ca–Fe-60, Mg–Al-450, etc. In case of MgCa–M^{III} LDHs, the molar ratio of Mg to Ca was 1:3, 1:1 and 3:1, while the molar ration of $[Mg + Ca]/M^{III}$ was kept at 2:1. All the nitrate salts (AR grade) i.e. $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were from Fisher Scientific, UK.

2.2. Test solution

2.2.1. Working solution

The working adsorbate solution with desired concentration for all experiments was freshly taken from the phosphate stock solution of 50 mg P/L, which was prepared by dissolving AR grade $NaH_2PO_4{\cdot}H_2O$ into deionized water. The pH of the working solutions was adjusted manually to the given values by diluted NaOH or HCl solutions.

2.2.2. Effluent

This was collected from Shieldhall Waste Water Treatment Works in Glasgow, Scotland (UK) and the sampling unit was the discharge point to the river. The quality parameters of the effluent sample are given in Table 1.

2.3. Phosphate uptake assays

The sorption experiments for phosphate (as total P) uptake were carried out at room temperature in 50 mL screw-top centrifuge tubes by adding various doses of LDH compounds and 25 mL of adsorbate solution with initial total P concentration of 10 mg/L and pH ~ 7. The mixing of LDH and adsorbate solution was performed by using an eight-arm flask shaker (SF1, Stuart) for 20 h at 800 rpm. However, this shaker was replaced after preliminary run at various doses of different LDHs by a rotary shaker (Rotator SB3, Stuart), which was operated at a maximum rotation speed of 40 rpm with the tube holder in 45° angular position. After appropriate shaking time, the suspension was immediately centrifuged for phase separation and the supernatant pH was measured. Finally, the supernatant was collected through filtration using syringe filter (0.45 μm Whatman filter disc) and analysed to determine the residual P concentration. The same procedures were applied while determining the equilibrium time of shaking and the time intervals were 0.25, 0.5, 1, 2, 3 and 4 h. In this case, the initial P concentration and solution pH were fixed at 10 mg/L and 7, respectively, and the adsorbent dose was 0.3 g/L. Moreover, P adsorption study with selected LDHs was performed under different initial total P concentrations (5–50 mg/L) and initial pH levels (3–12). The shaking time was used 2 h in both the cases, while the adsorbent dose and other procedures remained constant as mentioned. Later, sorption studies were carried out with MAXQ 4450 orbital shaker (Thermo Scientific) at 250 rpm, and the reproducibility of the results were checked and justified with those obtained by rotary/eight-arm flask shaker.

Table 1
Effluent quality characteristics

Quality parameters	Values at different collection times	
	15 May 2012	01 October 2012
pH	7.3	6.8
Turbidity (NTU)	3	1
Total suspended solids (mg/L)	6.1	1.8
Soluble P (mg/L)	3.6	1.4
COD (mg O_2/L)	27	27
Total N (mg/L)	NM[a]	3.7

[a]NM: not measured.

2.4. Analytical approach

All the pH measurements were carried out with a Hanna checker pH meter and this was calibrated with buffers of 4.0, 7.0 and 9.2 before any measurement. The Ohaus Analytical Plus balance was used for any weighing purpose, which can measure to the nearest of 0.1 mg. The P concentration was determined by a UV/vis spectrophotometer (Jenway 6505) at absorbance 880 nm, following the ascorbic acid method [21]. The adsorption capacity (Q_e, mg/g) or the amount of P adsorbed by the LDH and the removal rate (R) of P were calculated from the following relations:

$$Q_e = \frac{(C_o - C_e) \times V}{m}, \quad R\,(\%) = 100 \times \frac{C_o - C_e}{C_o}$$

where C_o is the initial concentration of the P (mg/L), C_e is the equilibrium or residual P concentration (mg/L), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

The concentration of total nitrogen in the supernatant, after phosphate uptake, was measured by photometer 7100 (Palintest Ltd, UK) using Palintest

reagents following persulphate oxidisation method [21]. To characterize LDHs, Ca/Al–NO_3-60 was used before and after phosphate adsorption. Phosphate-loaded LDHs were obtained via the process of adsorption, filtration (to separate solids), washing by deionised water and drying at 105℃ overnight. The dissolution of LDHs was checked by determining the difference between mass of LDHs before and after adsorption. The morphology of the LDH samples was examined by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy analysis unit.

3. Results and discussion

3.1. Screening of LDHs and optimal dose in phosphate sorption

From the preliminary studies with all synthesised LDHs at various doses, it was observed that the adsorption of phosphate on Ca-based (e.g. Ca-Al, Ca-Fe) or Ca-dominated (e.g. Mg_1Ca_3-Al, Mg_1Ca_3-Fe) LDHs was appreciably higher than those on Mg-based LDHs. Moreover, LDHs synthesized at 450℃ were not found to improve the sorption performance. Further studies with all LDHs under the same experimental conditions (i.e. adsorbent dose 0.3 g/L, $[P_o] \sim 10.3$ mg/L, $pH_o \sim 7$, $T = 2$ h) confirmed the above findings as shown in Table 2, because the removal of phosphate followed a clear decreasing trend on Mg-based LDHs or when the proportion of Mg increased in the MgCa–(Al or Fe)–LDH.

The phosphate removal with Ca-based LDHs was 97–99%, whereas the removal with Mg-based/dominated LDHs was <50% (Table 2). In terms of the preliminary results as stated above, four Ca-based LDHs (synthesized at 60℃) were selected to study the effect of adsorbent dose as shown in Fig. 1. The optimal adsorbent dose was 0.3 g/L, as with higher dose no significantly higher removal was observed. The corresponding adsorption amount was 33–34 mg-P/g (Fig. 1). But sorption capacity was decreased with increasing dose, with the maximum sorption capacity of 71 mg/g observed at 0.1 g/L dose on Ca–Al–LDH60. This can be attributed to the availability of surplus or overlapping active site sites at higher dosage as observed in other studies as well [16].

Table 2
Various synthesized LDHs for phosphate sorption study (adsorbent dose = 0.3 g/L, pH 7 and $T = 2$ h)

Removal of phosphate (%) from 10 mg PO_4-P/L solution (± SD)			
	LDHs synthesized at		Calcined LDHs
LDHs	60℃	450℃	
Ca–Al(NO_3)	99.1 ± 0.3	99.5 ± 0.0	99.3 ± 0.1
Ca–Fe(NO_3)	99.2 ± 0.3	99.0 ± 0.2	–[a]
Ca–Fe(Cl)	97.8 ± 0.4	–	97.2 ± 1.0
Mg–Al(NO_3)	17.9 ± 4.4	2.6 ± 0.4	–
Mg–Fe(NO_3)	14.3 ± 2.0	22.4 ± 2.0	–
Mg_1Ca_1–Al(NO_3)	85.9 ± 2.9	42.7 ± 1.3	–
Mg_1Ca_1–Fe(NO_3)	68.1 ± 2.1	68.8 ± 2.0	–
$Mg_{1.5}Ca_{0.5}$–Al(NO_3)	38.7 ± 1.8	46.6 ± 0.7	–
$Mg_{1.5}Ca_{0.5}$–Fe(NO_3)	28.6 ± 2.0	37.7 ± 1.7	–
$Mg_{0.5}Ca_{1.5}$–Al(NO_3)	97.9 ± 0.5	96.8 ± 0.4	–
$Mg_{0.5}Ca_{1.5}$–Fe(NO_3)	97.1 ± 0.7	98.3 ± 0.2	–

Notes: SD = standard deviation ($n = 3$).
[a]Data not available.

3.2. Effect of contact time

The adsorption, as a function of contact time at constant initial concentration ($[P_o] = 10$ mg/L), was conducted with selected LDHs and the results are presented in Fig. 2. It is seen that the equilibrium time required for the adsorption of P on all three LDHs was almost 2 h and the removal rate was about 98–99% by this time. No significant decrease in residual P concentration was observed with further increase in retention time after 2 h. So, all the further adsorption experiments were conducted at 2 h contact time.

3.3. Effect of adsorbate solution pH

The effect of different initial pH values ranging from 3 to 12 on the adsorption of P by selected LDHs is shown in Fig. 3. It shows that the rate of adsorption (~98%) was almost steady in the range of pH 3.5–10.5. With further increase in pH up to 12.0, there was a steady decrease. This is in conformity with two facts: (i) higher pH causes increasing competition for adsorption sites between OH^- groups and phosphate species and (ii) a higher pH can cause the adsorbent surface to carry more negative charges and thus, would enhance repulsive interaction between the adsorbent surface and the anions in solution [16,19]. Fig. 3(b) is revealing the strong buffering capacity of the selected LDHs, because the final pH remained about 10.5 for an initial pH of 3.5–10.5, with no significant changes observed in the removal rate for such a wide initial pH range. So, these results are suggesting the applicability of using Ca-based LDHs for phosphate removal under different pH systems.

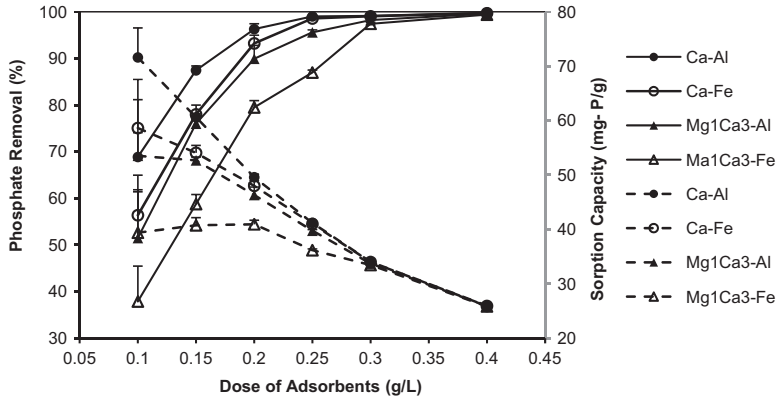

Fig. 1. Adsorption of phosphate on selective LDHs as a function of adsorbent dose. Solid and doted lines indicate the percentage of removal and sorption capacity, respectively. *Y* error bars indicate the standard deviation at each data point ($n = 5$ at dose 0.2 and 0.3 g/L and $n = 3$ for the rest of the dose).

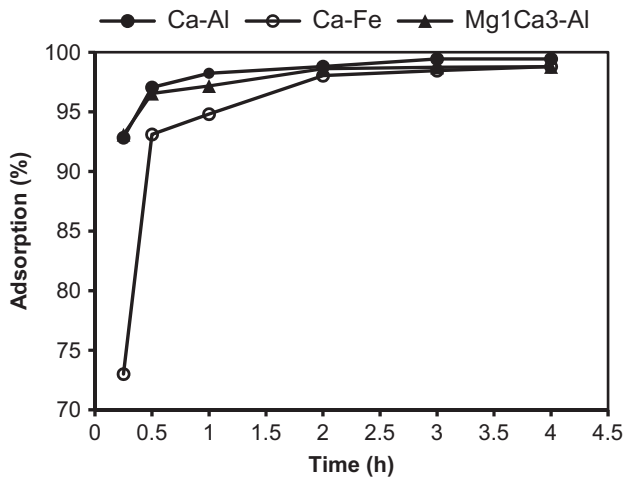

Fig. 2. Adsorption of phosphate on selected LDHs as a function of contact time (adsorbent dose = 0.3 g/L, $[P_o]$ = 10 mg/L and $pH_o \sim 7$).

3.4. Effect of initial phosphate concentration and adsorption isotherm

Selected Ca-based LDHs were further studied using the optimum dose (0.3 g/L) to investigate the effect of initial phosphate concentrations ($[P_o]$ = 5–50 mg/L) on the phosphate removal. The results showed that the removal of phosphate decreased substantially from 99 to 30% with increasing in $[P_o]$ from 5 to 50 mg/L. This could attribute to that for a fixed adsorbent dose, increasing in the phosphate concentrations will lead to the shortage of available numbers of active sites that can accommodate phosphate [16,22]. However, more than 85% removal was observed by the Ca–Al-based LDHs for the $[P_o]$ up to 20 mg/L.

The study data were used to plot linearly transformed Langmuir and Freundlich adsorption equation, and values of isotherm constants are presented in Table 3. The values of correlation coefficient are showing better fit to Langmuir equation than to Freundlich equation, indicating the better applicability of Langmuir isotherm equation to describe phosphate adsorption capacity. This is consistent with other studies in phosphate removal by LDHs [19,23]. The adsorption capacities of 66.7, 47.4 and 70.9 mg-P/g by Ca–Al, Ca–Fe and Mg_1Ca_3–Al LDH, respectively, determined by Langmuir isotherm model agreed well with the experimental equilibrium capacities of 69, 48.7 and 67.6 mg-P/g, respectively, and thereby, indicating the higher sorption capacity by Ca–Al-based LDHs. In Freundlich model, larger K_f indicates greater overall adsorption capacity, which also shows the higher capacity by Ca-Al-based LDHs. Although most researches have demonstrated that Langmuir adsorption equation is highly correlated with the phosphate-LDHs adsorption data, a good fitness of Freundlich isotherm equation to the phosphate removal by LDHs has been apparent from the coefficient values of n ($n > 1$) in this study.

3.5. Phosphate removal from real effluent

Real effluent, (both undisturbed and spiked up to ~10 mg-P/L), from wastewater treatment plant was used to study the P removal by Ca–Al-60 LDH and the results are shown in Fig. 4. It is clearly evident that effluent with low-to-high P concentration can be treated successfully by Ca–Al-60 LDH to meet the standard of discharge concentration, depending on the selection of suitable adsorbent dose. More than 90%

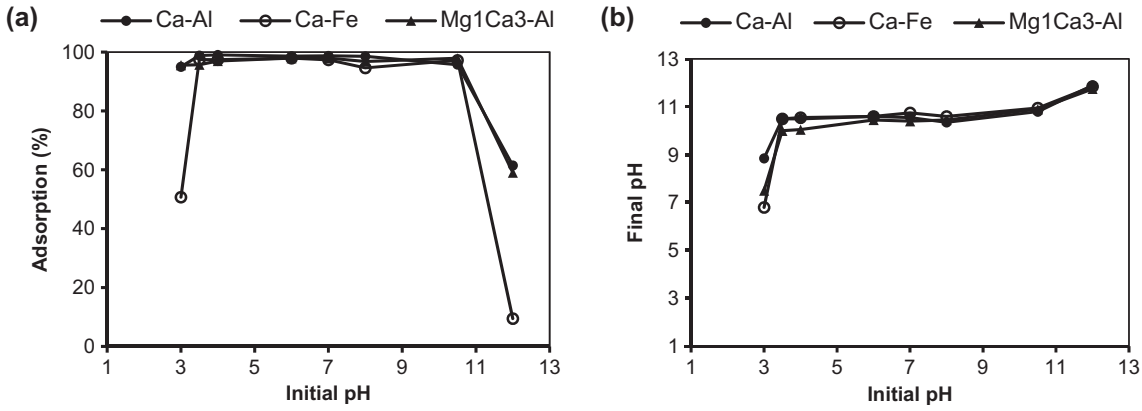

Fig. 3. (a) Effect of pH on the uptake of phosphate by selective LDHs and (b) final pH of the solution as a function of the initial pH (adsorbent dose = 0.3 g/L, $[P_o]$ = 10 mg/L and T = 2 h).

Table 3
Isotherm model constants for phosphate adsorption on selective LDHs

	LDHs		
	Ca–Al	Ca–Fe	Mg_1Ca_3–Al
Langmuir isotherm	$\left(\frac{1}{q_e} = \frac{1}{q_o b C_e} + \frac{1}{q_o}\right)$		
q_o (mg/g)	66.7	47.4	70.9
b (L/mg)	7.64	4.6	4.99
R^2	0.9972	0.8801	0.9829
Freundlich isotherm	$\left(\log q_e = \log K_f + \frac{1}{n}\log C_e\right)$		
K_f	43.7	31.5	42.2
n	4.09	5.49	3.93
R^2	0.9124	0.5756	0.8856

Notes: q_o, maximum adsorption capacity (mg/g); b, adsorption equilibrium constant (L/mg); q_e, adsorption capacity at equilibrium (mg/g), C_e, equilibrium adsorbate concentration (mg/L); K_f and n are the Freundlich isotherm constants.

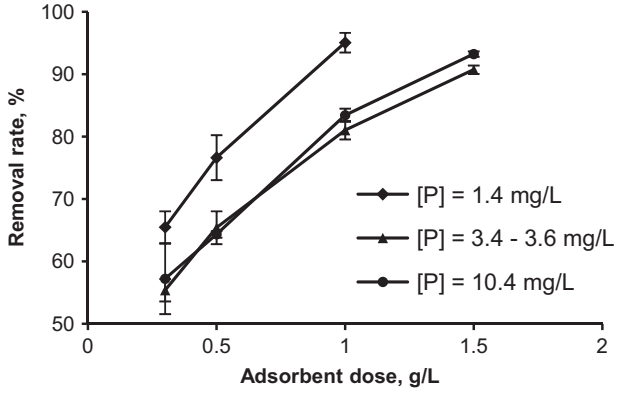

Fig. 4. Phosphate uptake from effluent with different starting P concentrations as a function of dose (pH_o = 7.1 ± 0.4, T = 2 h). Y error bars indicate the standard deviation at each data point (n = 2).

removal of P was observed at 1.5 g/L adsorbent dose for effluent P concentration of 3.4–10.4 mg/L (Fig. 4).

3.6. SEM image and composition analysis

SEM equipped with secondary and back-scattered electron detectors, an energy-dispersive x-ray system, a cryogenic stage, and a cathodoluminescence detector. The image of two LDH samples can be seen in Fig. 5.

Ca–Al–NO_3 LDH has smaller size and looser structure before phosphate sorption in comparison with that after taking phosphate. Decreasing in contents of nitrogen and sodium with increasing in phosphorous in the used LDH (Table 4) indicates that anion exchanges between NO_3^- and PO_4^{3-} took place and some Na released into the liquid phase. Releasing nitrogen and sodium from the Ca–Al–NO_3 LDH into

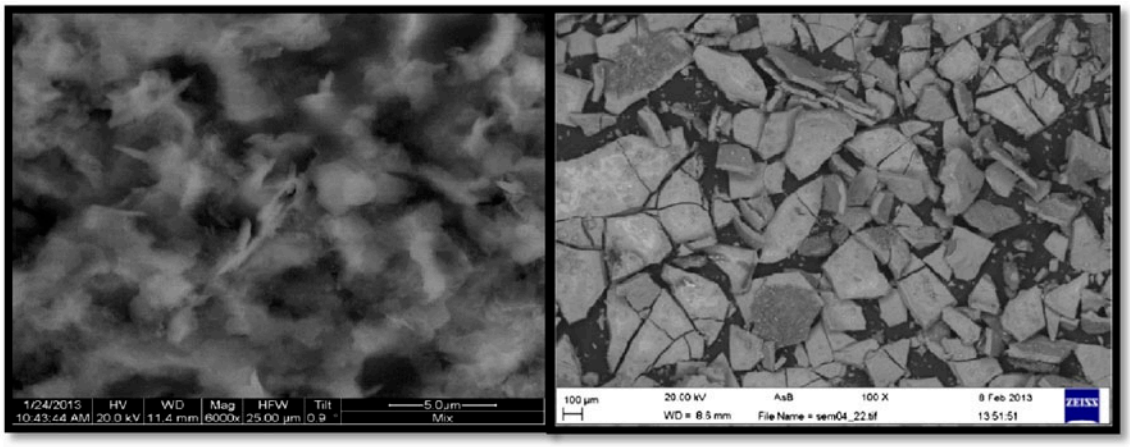

Fig. 5. SEM images of Ca–Al–NO_3 LDH before (left) and after (right) phosphate sorption.

Table 4
Variation of element (%) in the Ca–Al–NO_3 LDH before and after phosphate sorption

Element	Before sorption	After sorption
N	18.17	0
O	51.41	50.90
Na	21.37	13.60
Al	6.73	3.50
Ca	2.32	23.70
P	0	8.3
Total	100	100

the effluent suggests that such type of LDHs might not be suitable to be used in practice and more researches are needed to study LDHs' leachate composition as well as to investigate the other format of LDHs for the removal of phosphate from water and waste water.

4. Conclusions

The results of the present study indicate that nitrate-intercalated Ca-based LDHs can remove significantly higher phosphate than Mg-based LDHs from aqueous solution. The adsorption data fitted with Langmuir isotherm and accordingly, the maximum sorption capacity is in the range of 66.7–70.9 mg-P/g, which agreed well with those under experimental equilibrium (67.6–69 mg-P/g) by Ca–Al–NO_3-based LDHs. The study suggested that these LDHs were not affected by the different pH conditions. Moreover, the results demonstrated that the real effluent from a wastewater treatment plant with high P content (3.4–10.4 mg/L) can be treated with >90% removal by Ca–Al-60 LDH to meet the standard of discharge concentration. Future study is suggested to study LDHs' leachate composition as well as to investigate the other format of LDHs for the removal of phosphate, to identify the recyclability of CaMg-based LDH and recovery of phosphate with the consideration of practical applicability.

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