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Study on the sorption-desorption-regeneration performance of Ca-, Mg- and CaMg- based layered double hydroxides for removing phosphate from water

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ABSTRACT

Various layered double hydroxides (LDHs) were prepared by the co-precipitation method using the most common divalent and trivalent metal precursors. The resulting LDHs were studied for their performance in removing phosphate from aqueous test solution. The results have clearly demonstrated the influence of Ca and Mg as pre-cursor metals in synthesizing LDH compounds for removing phosphate. For the same LDH's dose, more phosphorus was removed by Ca-based LDHs than Mg-based LDHs. Real effluent from a wastewater treatment plant with high phosphate concentration (3.4 – 10.4 mg-P/L) can also be treated with >90% removal by both Ca- and Mg-based LDHs depending on the selection of suitable dose. For Ca-based LDHs, the main removal process was observed to be as calcium-phosphate precipitation. Due to the loss of layered structure after first sorption/precipitation operation, Ca-(Fe or Al)-LDHs cannot be regenerated for reuse. However, Mg-based LDHs showed potentially applicable for the regeneration and reuse due to their stable nature in aqueous phase than Ca-based LDHs. On the other hand, when choosing CaMg- based LDHs for the phosphorus removal, the nature of Ca dissolution from such LDHs needs to be taken

into account although they were demonstrated to be reusable with the efficiency of phosphate removal up to 64% at the fourth cycle.

Keywords: layered double hydroxide (LDH), phosphate removal, sorption, desorption, regeneration, anion exchange, ion release

1. Introduction

Excess phosphorus (P) in lakes, lagoons and rivers is one of major causes of eutrophication (known as the process to extensive growth of water plants, algae, and plankton), because it is an essential, often limiting, nutrient for growth of phototropic organisms in most ecosystems [1]. A minimal amount of phosphorus in water, even at phosphate concentration of 0.5 mg/L, with the availability of carbon and nitrogen at C:N:P molar ratio of 105:15:1 can cause substantial algae growth [2,3], and thereby, subsequent deterioration of water quality like depletion of oxygen, production of toxin from some harmful algal blooms, loss of aesthetic value of water body, etc. can occur. The global surface water bodies such as rivers and streams, lakes and reservoirs, and estuaries are facing the risk of eutrophication. For example, the symptoms of eutrophication is likely in about 78% and 65% of the coastal areas of United States (U.S.) and European Union (EU), respectively, and the economic loss due to eutrophication of freshwaters have been estimated at \$2.2 billion annually in the U.S. alone [4]. Phosphorus is often found in municipal and some industrial wastewaters as organic phosphate, inorganic phosphate, oligophosphates and polyphosphates (particular P). An approximate concentration of total P in a typical raw wastewater is 10 mg-P/L with ortho-phosphate as the principal form of phosphate [5]. So, to meet the standard of water quality, it is essential to remove phosphate prior to discharge of wastewater effluents into natural water bodies. According to the European Union (EU) Urban

Wastewater Treatment Directive (91/271/EEC), the required discharge concentration of total P in the final effluent should not exceed 2 mg/L in an area with a population equivalent (p.e.) of between 10000 and 100000, and not exceed to 1 mg/L when the p.e. >100000 [6]. In order to limit eutrophication, U.S. guidelines recommend the maximum total P concentrations of 0.05–0.1 mg-P/L in streams and 0.025 mg-P/L in lakes and reservoirs [7].

The major treatment processes to remove and recover phosphate from wastewaters include ion exchange, chemical precipitation, biological treatment, crystallisation and adsorption [2, 8–10]. 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 [9]. 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 [10]. 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, aluminum salts, etc. However, many of such sorbent materials were not found to be satisfactory in terms of achieving good adsorption capacity, reusability and compatible applicability to traditional wastewater treatment plants (e.g. pH, contact time) and hence, these were not used widely [10,11]. So, the research in the recent years has focused on developing efficient adsorbents with high sorption capacity and recyclability, 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 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 [5,16]. Very few study 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 to 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 recent years, researches have been made to use LDH for the removal of phosphorus. Super-paramagnetic microparticles modified with LDH were studied as phosphate adsorbers. [21,22]. Magnetic separation and chemical regeneration of the particles allows their reuse, leading to the successful recovery of phosphate. In another

study [23], Zr⁴⁺ incorporated MgAl –LDHs with different molar ratios of Mg/(Al + Zr) were prepared to assess their uptake behavior toward phosphate ions. The large uptake and high selectivity of the CO₃-type tertiary LDHs is well explained by complex formation of phosphate ions directly with Zr(IV) centers in the layers.

In the present study, rather than using Zr- incorporated and CO₃-type tertiary LDHs, a number of NO₃⁻ and Cl⁻ intercalated LDHs were prepared using the most common divalent and trivalent metal precursors (Mg²⁺, Ca²⁺, Fe³⁺ and Al³⁺) in order to study the performance of these LDHs in removing phosphate from aqueous solution. As well as the performance assessment, this research investigated the potential of the reuse of these materials for phosphate removal and thereby attempts to enhance the limited knowledge on the synthesis, regeneration and use of LDHs for sustainable phosphate uptake from water.

2. Materials and experimental procedures

2.1. Synthesis of LDH compounds

Based on the combination of divalent (M^{II}: Mg²⁺, Ca²⁺) and trivalent (M^{III}: Al³⁺, Fe³⁺) cations such as Mg-Al, Ca-Al, Mg-Fe, Ca-Fe, CaMg-Al and CaMg-Fe, and two drying temperatures (60 and 450°C), a number of different LDHs were prepared by the coprecipitation method, following a method described in [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°C 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 1500 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°C for 24 h and 450°C for 2 h, respectively. Finally, the dried LDH compounds were crushed to powders and stored in screw-top 22 mL glass vial kits. In case of CaMg-M^{III} LDHs, the molar ratio of Ca to Mg was 1:3, 1:1 and 3:1, while the molar ratio of [Mg+Ca]/ M^{III} was kept at 2:1. LDHs synthesized with either Ca or Mg as only or dominating divalent precursor will be denoted as Ca-based and Mg-based LDHs, respectively. Considering the removal performance of Ca-based LDHs, another set of Ca-Al-60 LDH was synthesized to check the reproducibility of the findings. Also some portion of it was calcined at 450°C for 2 h to identify any potential difference in removal performance in comparison to that synthesized at 450 °C as the drying temperature. In addition to the above NO₃⁻ intercalated LDHs, Cl⁻ intercalated Ca-Fe(Cl)-60, Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-60 and Mg-Fe(Cl)-60, and their calcined products were also synthesized to study any influence of interlayer anion on P removal. All the nitrate and chloride salts (AR grade) i.e. Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, CaCl₂·6H₂O and FeCl₃·6H₂O were from Fisher Scientific, UK.

2.2. Adsorbate solution

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 NaH₂PO₄·H₂O into deionized water. The pH of the working solutions was adjusted manually to the required values by diluted NaOH or HCl solutions.

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

Table 1: Effluent quality

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 into 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 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 by using syringe filter (0.45 µm Whatman filter disc), and analysed to determine the residual P concentration. In this way, preliminary sorption runs were conducted to select appropriate LDHs and their dose. Then, to determine the equilibrium contact time of mixing for the selected LDHs, the initial P concentration and solution pH were fixed at 10 mg/L and 7, respectively. Moreover, P adsorption study with selected LDHs was performed under different initial total P concentrations and at various initial pH levels to determine the adsorption isotherms and the effect of pH, respectively. Partly, sorption studies were also carried out with MAXQ 4450 orbital shaker (Thermo Scientific) at 250 rpm due to its capacity to hold large number of samples, and the reproducibility of the results were checked (within 3% variation) with that obtained by rotary

shaker. In summary, the sequence to select the best LDHs for the removal of phosphorus started with screening the type and dose of LDHs, was followed by the kinetics studies of the phosphorus sorption and anion exchange, and then the investigations on the effect of solution pH and start P concentration on the phosphorus removal performance.

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 [24]. The adsorption capacity (Q_e , mg/g) or amount of P adsorbed by the LDH and removal rate (R) of P were calculated from the following relations:

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

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 adsorbent (g).

Selected LDHs were characterized physicochemically before and after phosphate adsorption. Phosphorus-loaded LDHs (P-LDH) were obtained via the removal of phosphate from working adsorbate solution, filtration (to separate solids), washing by deionised water, and drying at 105°C overnight. To study the structural patterns of the LDHs, X-ray diffraction (XRD) analyses were performed on a Siemens D5000 Diffractometer, employing Cu Kalpha radiation with a step size of 0.02 degrees and a counting time of 1s per step. The measurements were run in the 2 theta range of 5-85 degrees, and samples were prepared by

compaction into a sample holder. The morphology of the LDH samples was examined by a scanning electron microscopy (SEM) equipped with secondary and back scattered electron detectors, an energy dispersive x-ray system (EDXs), a cryogenic stage, and a cathodoluminescence detector.

The concentration of various ions (e.g. Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Cl^- , NO_3^-) in the aqueous phase was determined by RFID enabled HACH DR3900 spectrophotometer using respective reagents from HACH LANGE, UK. While identifying ion release from LDH products, the supernatant was collected and analysed for required ions concentration followed by 2 h shaking of LDH contained adsorbate solution with subsequent centrifugation. Then the released mass of each ion in the known volume of supernatant was calculated, and thus based on the mass of input LDH and each released ion, the percentage of each ion released from the LDH products was determined.

2.5. Phosphate desorption and regeneration of LDH

Selected LDHs were studied for phosphate sorption-desorption-regeneration cycle. In the first cycle, phosphate sorption was conducted for 18 h in room temperature by mixing LDHs in adsorbate solution of concentration of 10 mg-P/L at appropriate dosage. Then, phosphate saturated LDHs (P-LDH) were separated through filtration and rinsing with deionized water, and subsequently mixed with NaOH at different concentrations to evaluate phosphate desorption (Fig. S1 in supplementary section). The desorption shaking was run for 20 h using the estimated volume of NaOH required to maintain the same dose in sorption study. Then, supernatant was collected followed by centrifugation and the extent of phosphate release was analysed. After desorption run, the resulting LDHs were separated, washed and regenerated by calcination at 450°C for 2 h. In this way, the selected LDH was regenerated up to fourth

cycle, and the selected desorbent was re-used in the subsequent cycles after used as desorbent in the first cycle.

The sorption rate (R_{ads}) and desorption rate (R_{des}) were estimated from the following relations:

$$R_{ads(i)} (\%) = 100 \times \frac{C_0 - C_{(i)}}{C_0}, \quad R_{des(i)} (\%) = 100 \times \frac{Q_{des(i)}}{Q_{ads(i)}}$$

where C_0 : initial concentration of P (mg/L); $C_{(i)}$: residual concentration of P in the i th adsorption operation (mg/L); $Q_{ads(i)}$: amount of P uptake in the i th adsorption operation (mg-P/g LDH); $Q_{des(i)}$: amount of P desorbed in the i th desorption operation (mg-P/g LDH). .

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, Ca_{1.5}Mg_{0.5}-Al, Ca_{1.5}Mg_{0.5}-Fe) LDHs was appreciably higher than those on Mg-based LDHs. Moreover, LDHs synthesized or calcined at 450°C were not found to improve the sorption performance significantly than those synthesized at 60°C. Further studies with all LDHs under the same experimental conditions (i.e. adsorbent dose 0.3 g/L, [P₀] ~10.3 mg/L, pH₀ ~7, T = 2 h) confirmed the above findings as shown in Fig. 1, because the removal of phosphate followed a clear decreasing trend in accordance of LDHs prepared with Mg²⁺ cation or with the proportion of this cation increased in the CaMg-(Al or Fe)-LDH.

The phosphate removal with Ca-based LDHs were 85–99%, whereas the removal with Mg-based LDHs were <50% under the same operating conditions (Table 2). These results

have clearly demonstrated the influence and selection of Ca and Mg as pre-cursor metals in synthesizing LDH compounds for removing phosphate. It was also interesting to observe that LDHs intercalated with Cl^- showed comparatively less removal percentage of phosphate than those intercalated with NO_3^- as seen from Table 2. So, the influence of interlayer anion in LDHs was in the order of $\text{NO}_3^- > \text{Cl}^-$ for higher phosphate removal. Based on the above results, further studies on the effect of adsorbent dose, contact time, pH and initial phosphate concentration were conducted with selected Ca-, Mg- and CaMg- based LDHs.

The effect of LDH's dose on phosphate adsorption is shown in Fig. 2. The optimal adsorbent dose was 0.3 g/L after mixing for 20 h, as with higher dose no significantly higher removal was observed. The corresponding adsorption capacity was 33–34 mg-P/g (Fig. 2). In general, Ca-Al-60, Ca-Fe-60 and $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Al-60}$ LDHs showed comparatively closer phosphate removal performance than that by $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe-60}$ between dose 0.1–0.3 g/L, however, the maximum sorption capacity of 71 mg-P/g was observed on Ca-Al-60. As expected, sorption capacity was decreased with increasing dose, because with increasing dose, the adsorbent mass was increased in the same volume of adsorbate solution while the mass of adsorbate to be sorbed remained same. In other words, this can be attributed to the availability of surplus or overlapping active sites at higher dosage as observed in other studies as well [5,16]. In comparison to the optimal adsorbent dose of Ca-based LDHs, Mg-based e.g. Mg-Fe(Cl)-LDHs were observed to require much higher optimal dose as 2 g/L to achieve about 99% removal of phosphate with sorption capacity of 5 mg-P/g.

Fig. 1. Phosphate removal trend as a function of using divalent cations (Ca or Mg-based). Y error bars indicate the standard deviation at each data point (n= 3).

Table 2

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

Fig. 2. Adsorption of phosphate on selective LDHs as a function of adsorbent dose. Solid and dotted lines respectively indicate the percentage of removal and sorption capacity. 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).

3.2. Effect of contact time and adsorption kinetics

The adsorption as a function of contact time at constant initial concentration ($[P_0] = 10$ mg/L) was conducted with selected LDHs and the results are presented in Fig. 3. It is seen that the equilibrium time required for the adsorption of P on those selected LDHs was almost 2 h and the removal rate was about 98–99% by this time. No significant decrease of 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.

Kinetic analyses on contact time were made by using first-order and Pseudo second-order kinetic model, and the model parameters are shown in supplementary Table S1. It can be seen that the correlation coefficients R^2 of pseudo second-order model are much higher than those of first-order model. Also, the theoretical uptakes q_e (cal) are in good agreement with the experimental uptakes q_e (exp) for the pseudo second-order model. So, the adsorption kinetics of phosphate by the selected Ca-, Mg- and CaMg- based LDHs are well governed by the pseudo second-order kinetic model.

Fig. 3. Adsorption of phosphate on selected LDHs as a function of contact time (adsorbent dosage was 0.3 g/L for Ca-based LDHs and 2 g/L for Mg-Fe(Cl)-450, $[P_o] = 10$ mg/L, $pH_o \sim 7$).

3.3. Effect of adsorbate solution pH

The effect of different initial pH values ranging from 3 to 12 on the adsorption of phosphate by selected LDHs is shown in Fig. 4. It shows that the rate of adsorption for Ca- and CaMg- based LDHs was almost steady (~98%) in the range of pH between 3.5–10.5 (Fig. 4a), whereas for Mg-Fe(Cl)-450, it was at pH between 3–7.5. 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. 4b is revealing the strong buffering capacity of the Ca-based LDHs, because the final pH remained about 10.5 for an initial pH range of 3.5–10.5, with no significant changes observed in 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 system.

Fig. 4. (Top) Effect of pH on the uptake of phosphate by selected LDHs; (Bottom) Final pH of solution as a function of initial pH. (adsorbent dosage was 0.3 g/L for Ca-based LDHs and 2 g/L for Mg-Fe(Cl)-450, $[P_o] = 10$ mg/L, $T = 2$ h).

3.4. Effect of initial phosphate concentration and adsorption isotherm

The effect of initial phosphate concentration on its adsorption by selected LDHs was studied at optimum adsorbent dosage (0.3 g/L for Ca-based LDHs and 2 g/L for Mg-Fe(Cl)-450). Generally, removal rate of phosphate decreased with the increase of initial concentration. The reason of such reduction in phosphate adsorption can be explained by the lack of available number of active sites that can accommodate increased phosphate species at fixed adsorbent dose [16,25].

The study data were used to plot linearly transformed Langmuir and Freundlich adsorption equation, and values of isotherm constants are presented in supplementary Table S2. It can be seen that 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 by Ca-, Mg- and CaMg- based LDHs. This is consistent with other studies in phosphate removal by LDHs [e.g., 19,26]. Moreover, Fig. S2 in supplementary section shows that model data determined by Langmuir model agreed better with the experimental data in comparison to those determined by Freundlich model. The adsorption capacity of phosphate on Ca- and CaMg- based LDH is much higher than that on Mg-based LDH, e.g. the maximum adsorption capacity on Ca-Al(NO₃)-60 is 66.7 mg-P/g, while on Mg-Fe(Cl)-450 is only 9.8 mg-P/g. In Freundlich model, larger K_f indicates greater overall adsorption capacity, which also shows the higher capacity by Ca-based LDHs than Mg-based LDHs. Nonetheless, a good fitness of Freundlich isotherm equation to the phosphate removal has also 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- and Mg- based LDHs (e.g. Ca-Al(NO₃)-60 and Mg-Fe(Cl)-450) and the results are shown in Fig. 5. It is clearly evident that effluent with low to high P concentration can be treated successfully by both type of LDHs to meet the standard of discharge concentration, depending on the selection of suitable adsorbent dose. More than 90% removal of P was observed by Ca-Al(NO₃)-60 at 1.5 g/L adsorbent dose from effluent with P concentration of 3.4–10.4 mg/L, while Mg-Fe(Cl)-450 removed about 98% at adsorbent dose of 4 g/L from effluent with 5.6 mg-P/L (Fig. 5).

Fig. 5. Phosphate uptake from effluent with different starting P concentration as a function of dose (pH₀ = 7.1±0.4, T = 2 h). Solid and dotted lines respectively indicate the removal by Ca-Al(NO₃)-60 and Mg-Fe(Cl)-450.

3.6. Physicochemical features of LDHs and their phosphate uptake process

The structural characteristic of the LDHs (before and after phosphate removal) were analysed by the powder X-ray diffraction (XRD) patterns as presented in Fig. 6. The XRD pattern of the as-synthesized sample Ca-Al(NO₃)-60 LDH (Fig. 6a) is similar to those of Ca-based layered materials i.e. hydrocalumite, e.g. Ca₂Al(OH)₆NO₃·2H₂O [27,28]. The characteristic diffractions (e.g. sharp, symmetric, strong lines at low 2θ values and weaker, less symmetric lines at high 2θ values) of hydrotalcite-like structure and easily recognizable Bragg reflections by typical planes of (003), (006), and (110) demonstrated the formation of LDH phase in CaAl(NO₃)-60. However, the phosphorus loaded P-Ca-Al(NO₃)-60 LDH did not show the XRD pattern of its original LDH structure after P removal (Fig. 6b). There was a significant loss of order of mixed oxide (Ca_xAl_yO) phases in P-CaAl(NO₃)-60, as observed by the broad peak at 2θ=25°–50°. Since ion exchange process of removing P suppose to retain

the hydrotalcite structure of the original Ca-Al(NO₃)-60 LDH as observed for other LDHs (e.g. Mg-Al(CO₃)-LDH) than Ca-based [16], so it is believed that there was a formation of amorphous precipitate during P removal. Therefore, P removal by Ca-Al(NO₃)-60 LDH was predominantly due to precipitation as calcium-phosphate (Ca-P) and this was also reflected from the composition analysis before and after P removal (Table 3). These findings of the present study are in conformity with the removal mechanism of Ca-based LDHs for removing different P species in other previous studies [3,29,30].

Fig. 6. Powder XRD patterns of two LDHs before (as-prepared) and after P removal.

On the other hand, the effect of calcination at 450°C is visible from the XRD patterns of Ca-Fe(Cl)-450 LDH (Fig. 6c), where the peaks of hydrotalcite structure are absent due to the collapse of layered structure. The diffraction patterns at higher 2θ values (27°–84°) suggest the formation of Ca-Fe mixed oxide (Ca_xFe_xO) phases, and thus indicate the decomposition of Ca-Fe(Cl)-LDH into a mixture of Ca-Fe oxides when heated at 450°C. In principle, it is expected that calcination at 450–500°C would lose the layer structure of LDHs and produce intermediate non-stoichiometric metal oxides, which in contact with aqueous medium regain the hydrotalcite structure through rehydration and sorption of anions [5,14]. But the calcined Ca-Fe(Cl)-450 LDH after removing P did not follow this hypothesis, rather a broken LDH structure with mixed oxide (Ca_xFe_xO or CaO) phases was observed, as evident from the XRD patterns of P-CaFe(Cl)-450 (Fig. 6d) similar to P-Ca-Al(NO₃)-60. The same trend was also observed by calcined Ca-Al(NO₃)-450 LDH and thereby, indicates that P removal process with these calcined LDHs was not different from their uncalcined forms such as Ca-Al(NO₃)-60 or Ca-Fe(Cl)-60 LDH but precipitation of Ca-P. This may be an indication that calcined

Ca-Al or Ca-Fe LDHs cannot be reused and recycled due to their inability to recover LDH structure.

Table 3: Variation of element in the CaAl(NO₃)-60 LDH before and after phosphate uptake.

An example of elemental analysis by SEM-EDXs before and after P removal can be seen in Table 3. Since hydrogen can not be displayed by the SEM-EDXs analysis, the element percentage was modulated to reach to 100 (Table 3). The decreasing portion of nitrogen with increasing phosphorus portion in the used LDH (i.e. P-Ca-Al(NO₃)-60) could be an indication that anion exchanges between NO₃⁻ and PO₄³⁻ took place. But the significant presence of calcium in the used LDH reveals that calcium-phosphate precipitate was formed during removal process, which is also indicated by the XRD pattern changes before and after phosphate uptake. However, the reduced portion of sodium and aluminium in the used LDH indicates their release into the liquid phase.

Furthermore, the instability of Ca-based LDHs is evident from Table 4 due to the occurrence of major ion release, with 32–53% mass loss for LDHs synthesized with Ca as the only divalent precursor (Ca-LDH). In particular, the release of interlayer anion from all the different LDHs was observed to be dominating as seen from Table 4, which is expected due to the anion exchange properties of LDHs. However, this release was observed to be much higher from LDHs intercalated only with NO₃⁻ than LDHs intercalated with Cl⁻ or both Cl⁻ and NO₃⁻. Since nitrogen release into surface water bodies is not either expected as phosphorus, so it can be suggested that NO₃⁻ may not be suitable to be intercalated with LDHs particularly when considering their application for wastewater treatment. It was noticeable that ion release or mass loss was reduced in case of Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃) and

Mg-Fe-LDHs. For example, Mg-Fe(Cl)-LDHs showed the lowest ion release tendency as seen from Table 4. This might be related to the presence of divalent cations i.e. Ca, Mg in the composition of LDHs, because Ca-LDHs have tendency to be more dissolute in the liquid phase than LDHs synthesized with Mg or both Ca and Mg as divalent precursor due to the higher solubility product of $\text{Ca}(\text{OH})_2$ ($K_{sp}= 5.02 \times 10^{-6}$) than $\text{Mg}(\text{OH})_2$ ($K_{sp}= 5.61 \times 10^{-12}$) [30]. So, the above findings again confirming that released Ca^{2+} from Ca-based LDHs is readily available to precipitate with phosphate, and the dissolution phenomena of Ca-LDH is responsible for losing LDH structure after P removal. However, it is believed that the layered structure can be retained in Ca-based LDHs when synthesized with both Ca and Mg as divalent precursors, as reflected from less ion release nature (Table 4) and regeneration capacity (described in section 3.7) of $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)\text{-LDH}$. So, the P uptake process on this LDH is expected as a combination of anion exchange and precipitation, which was also observed in some previous studies [29,30].

3.7. Desorption and regeneration

To select appropriate desorbent solution, different concentrations of NaOH were evaluated based on the desorption rate of P from P-LDH as shown in supplementary Fig. S1. However, in the preliminary trials, NaCl and combination of NaCl and NaOH were also evaluated at different concentrations (5–20%). But the P desorption rate with NaCl based solution was very lower compared to that of NaOH alone under the same concentration range. Then, according to the increasing desorption trend as seen in Fig. S1, 20% and 4% of NaOH were selected as desorbent solution to be used by $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)\text{-450}$ and Mg-Fe(Cl)-450, respectively, for regeneration studies. No previous studies were conducted on the desorption-regeneration performance of Ca-based LDHs; however, in a study with Zn-Al-300 LDH, Cheng et al., [26] also observed higher desorption rate of P with increasing

concentration of NaOH. But in their study 5% NaOH was adequate to achieve P desorption rate of about 88%, although further increase in concentration up to 20% NaOH could desorb P about 91%. The poor desorption rate observed by NaCl in this study is also in conformity with others [26,31], and it was reported that such a lower desorption rate by NaCl is expected due to the relatively low affinity of Cl⁻ with LDH compounds. But it is to be noted that LDHs can dissolve more with increasing concentration of NaOH, i.e. more ions can be released into liquid phase as observed in [26]. In spite of this phenomena, 20% NaOH was used in this study for consecutive regeneration cycles with Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-450.

Fig. 7. Sorption and desorption profiles of Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-450 at different cycles of regeneration. The values of line and bar diagrams are respectively assigned to left and right vertical axis. LDH indicates fresh material and LDH1-4 represent regenerated materials.

After first regeneration, phosphate sorption efficiency of Ca-Fe(Cl)-450 decreased significantly (to ~30%) due to disappearance of LDH structures as discussed in section 3.6, and therefore, regeneration and reuse of Ca-Fe(Cl)-450 were not considered for further studies. However, sorption, desorption and regeneration of Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-450 were investigated up to four regeneration cycles and results can be seen in Fig. 7.

In general, the P removal efficiency of Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-450 were decreased in the consecutive regeneration cycles from 95% to 64%. Although sorption capacity increased after first regeneration; with further operating cycles, it decreased from 19.3 to 12.5 mg-P/g of LDH. The accumulated adsorbed amount of P after four cycles of regeneration was about 42 mg-P/g of LDH. P desorption, however, remained above 85% throughout four cycles of regeneration; such consistent results suggest the possibility of re-using desorbent in consecutive desorption cycles.

The decreasing trend in phosphate removal efficiency by the regenerated $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)\text{-450}$ can be related to its ion release phenomena. The analysis of various ions in the supernatant after first adsorption-desorption cycle (Table 5) shows that after first regeneration following by adsorption and desorption operation, only about 41% of LDH mass remained. However, from second regeneration/reuse cycle, ion release was substantially reduced. This was in conformity with the dissolution nature of Ca^{2+} i.e. most of this cation was susceptible to be released during the first regeneration phase. So, in the subsequent regenerated products, $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)\text{-450}$ was potentially expected to be turned into Mg-based LDH, because the ion release data of Mg-based LDH (e.g. $\text{Mg-Fe}(\text{Cl})\text{-450}$) after adsorption-desorption operation shows that only about 7% of the LDH mass was lost (Table S3 in supplementary section). It can be mentioned that further ion release was below 1% after first regeneration. So, this is clearly demonstrating the better stable nature of Mg-based LDH than CaMg-based LDH. Since Mg-based LDHs were observed to require much higher optimal dose than Ca or CaMg-based LDHs in order to achieve similar P removal rate (as described in section 3.1), then it is expected that P removal rate with CaMg-based LDH in the subsequent regenerations will decrease. Therefore, Mg-based LDHs can be the potential choice for further investigation when regeneration and reuse of LDHs is concerned.

Table 5: Analysis of ions in the supernatant after adsorption-desorption operation.

4. Conclusions

The results of the present study indicate that Ca-based LDHs (e.g. $\text{Ca-Al}(\text{NO}_3)$, $\text{Ca-Fe}(\text{Cl})$, $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)$) can remove significantly higher phosphate than Mg-based LDHs (e.g. $\text{Mg-Fe}(\text{Cl})$, $\text{Mg-Al}(\text{NO}_3)$, $\text{Mg}_{1.5}\text{Ca}_{0.5}\text{-Al}(\text{NO}_3)$) from aqueous solution. Both NO_3^-

and Cl⁻ intercalated Ca-(Fe or Al)-LDHs showed the phosphate uptake of 97–99% at dosage 0.3 g/L from the aqueous solution with start P concentration of 10 mg-P/L, while Mg-(Fe or Al)-based LDHs showed much high dose required to achieve above 90% phosphate uptake. The adsorption kinetics of phosphate uptake by the selected Ca-, Mg- and CaMg- based LDHs are well governed by the pseudo second-order kinetic model and the equilibrium contact time reached at 2 h. The adsorption data fitted well with Langmuir isotherm and accordingly, the maximum sorption capacity on Ca_{1.5}Mg_{0.5}-Al(NO₃)-60 was 70.9 mg-P/g, while on Mg-Fe(Cl)-450 was 9.8 mg-P/g. The study on pH effect of adsorbate solution suggested that Ca-based LDHs can be potentially applied under a different pH system ranging between pH values of 3.5 to 10.5. Further, the results demonstrated that the real effluent from a wastewater treatment plant with high phosphate concentration (3.4–10.4 mg-P/L) can be treated with >90% removal by Ca- and Mg-based LDHs to meet the standard of discharge concentration, depending on the selection of suitable adsorbent dose. However, the physicochemical features of Ca-LDHs revealed that these are instable in aqueous phase and cannot be reused followed by adsorption, desorption and regeneration cycles due to loss of layered structure after first sorption operation. The P removal process with such LDHs is mainly due to calcium-phosphate precipitation and this could be the reason of their higher sorption capacity than Mg-based LDHs. But desorption-regeneration performance of Ca-based LDHs was improved when synthesized with both Ca and Mg as divalent precursors as observed with Ca_{1.5}Mg_{0.5}-Fe(Cl)(NO₃)-450 in this study. The regeneration and reusability of the CaMg- based LDH were demonstrated with phosphate removal efficiency up to 64% at the fourth cycle. However, the nature of Ca dissolution of such LDHs cannot be neglected. On the other hand, the demonstration of stable nature of Mg-based LDHs can be a direction to use such LDHs at high doses when regeneration and reuse is of importance.

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Appendix A. Supplementary material

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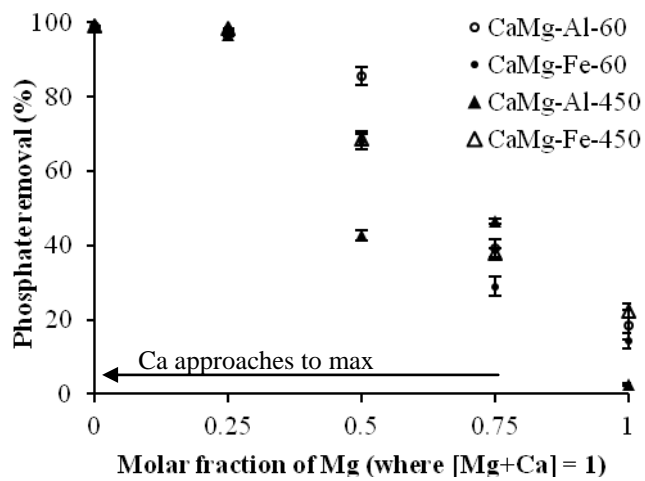


Fig. 1. Phosphate removal trend as a function of using divalent cations (Ca or Mg-based). Y error bars indicate the standard deviation at each data point (n= 3).

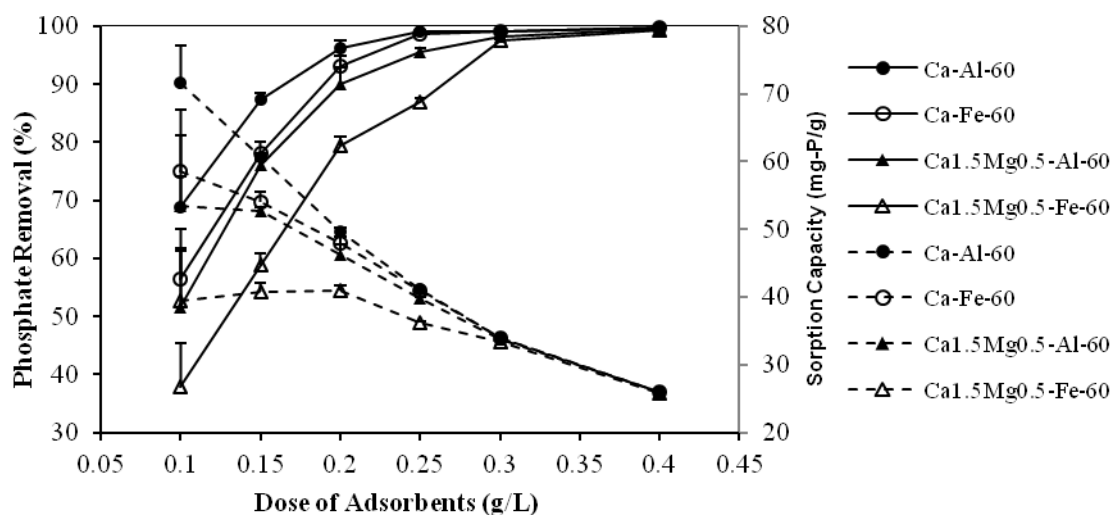


Fig. 2. Adsorption of phosphate on selective LDHs as a function of adsorbent dose. Solid and dotted lines respectively indicate the percentage of removal and sorption capacity. Y error bars indicate the standard deviation at each data point ($n = 5$ at dose 0.2 and 0.3 g/L, and $n = 3$ for the rest of the dose).

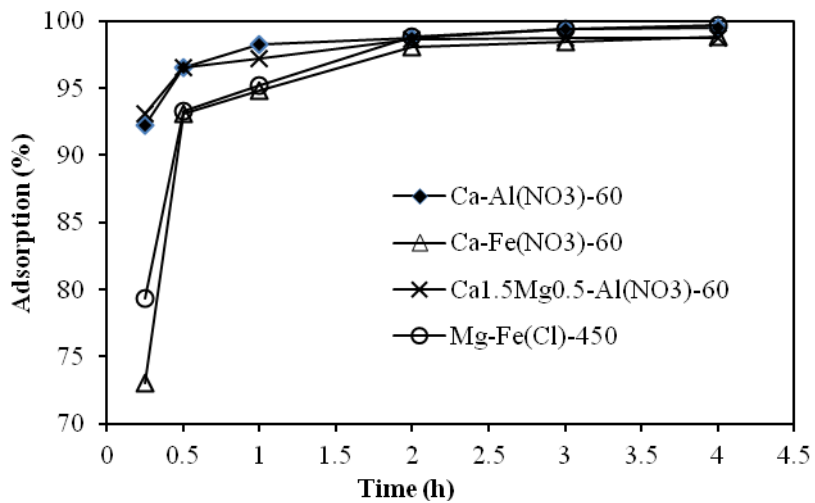


Fig. 3. Adsorption of phosphate on selected LDHs as a function of contact time (adsorbent dosage was 0.3 g/L for Ca-based LDHs and 2 g/L for Mg-Fe(Cl)-450, $[P_o] = 10$ mg/L, $pH_o \sim 7$).

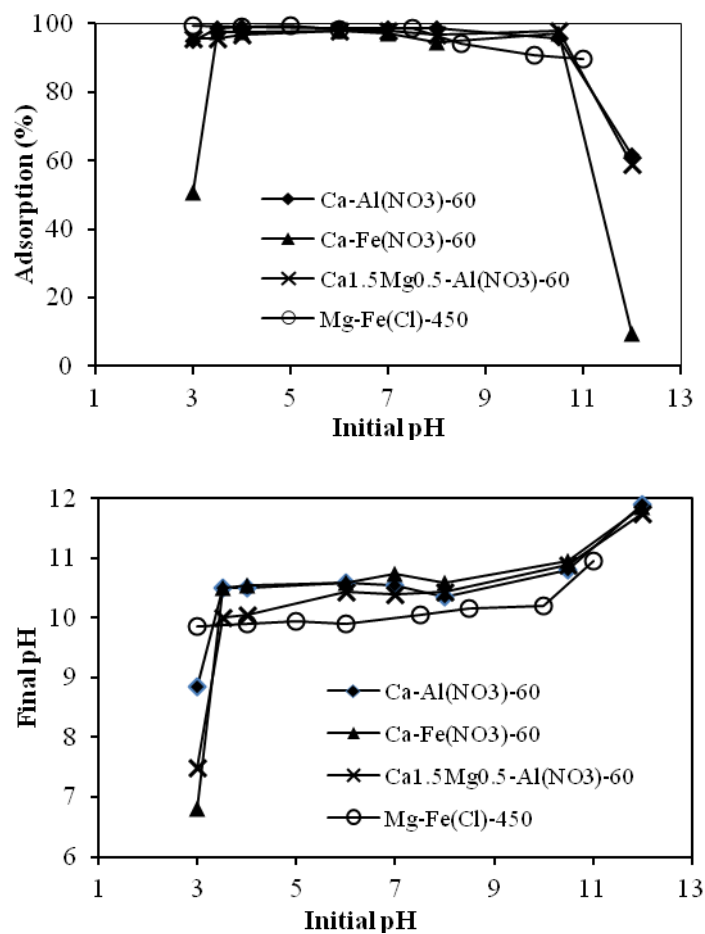


Fig. 4. (Top) Effect of pH on the uptake of phosphate by selected LDHs; (Bottom) Final pH of solution as a function of initial pH. (adsorbent dosage was 0.3 g/L for Ca-based LDHs and 2 g/L for Mg-Fe(Cl)-450, $[P_o] = 10$ mg/L, $T = 2$ h).

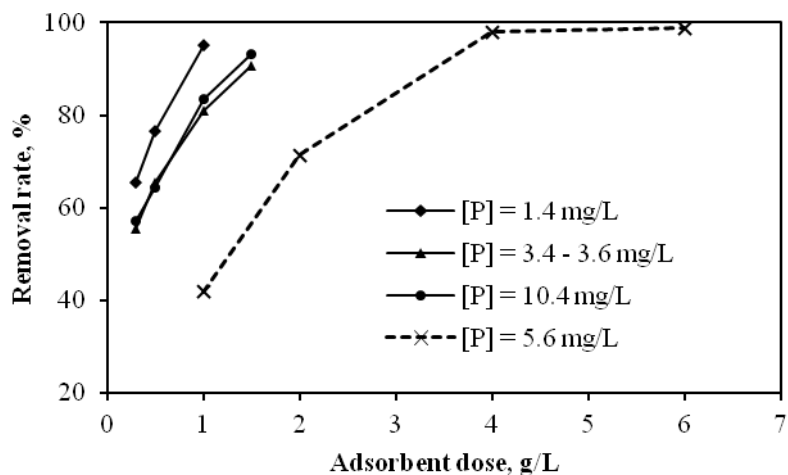


Fig. 5. Phosphate uptake from effluent with different starting P concentration as a function of dose ($pH_0 = 7.1 \pm 0.4$, $T = 2$ h). Solid and dotted lines respectively indicate the removal by Ca-Al(NO₃)-60 and Mg-Fe(Cl)-450.

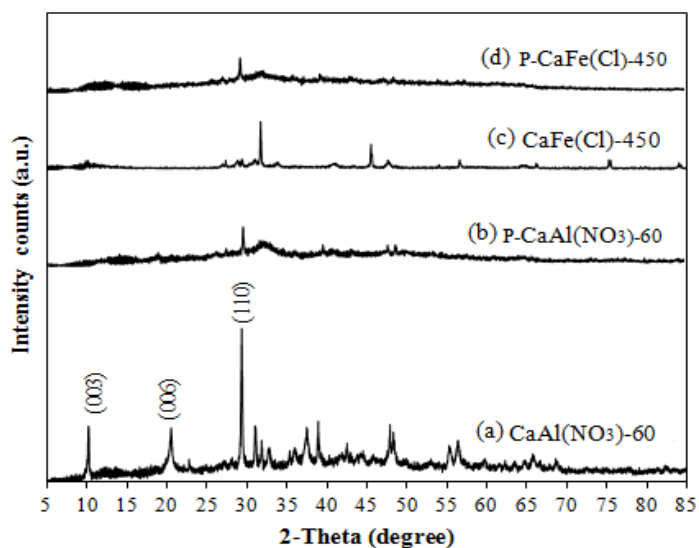


Fig. 6. Powder XRD patterns of two LDHs before (as-prepared) and after P removal.

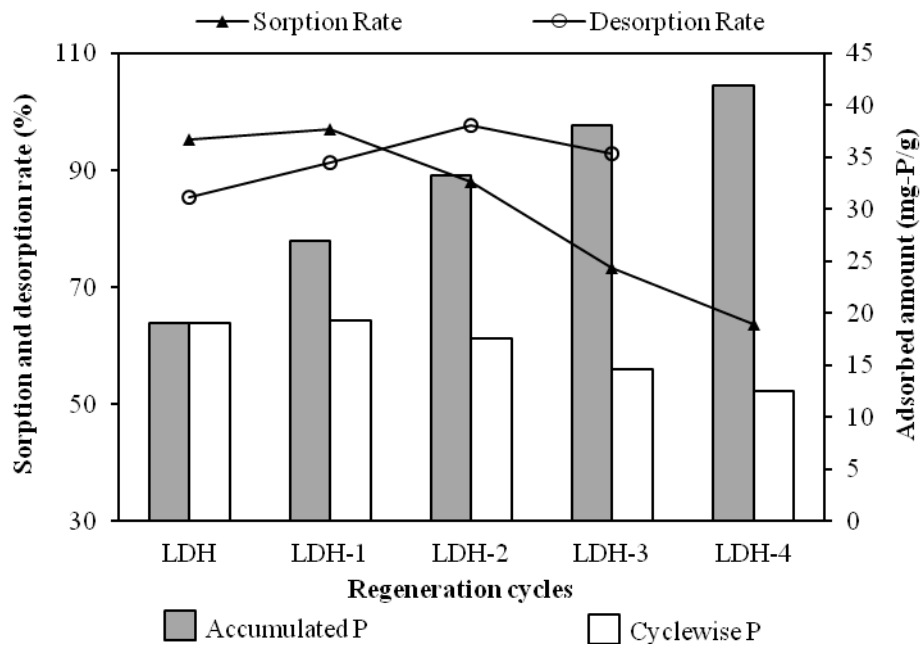


Fig. 7. Sorption and desorption profiles of $\text{Ca}_{1.5}\text{Mg}_{0.5}\text{-Fe}(\text{Cl})(\text{NO}_3)\text{-450}$ at different cycles of regeneration. The values of line and bar diagrams are respectively assigned to left and right vertical axis. LDH indicates fresh material and LDH1-4 represent regenerated materials.

Table 1

Effluent quality

Quality Parameters	Values at different		
	collection time		
	15.05.12	01.10.12	07.10.13
pH	7.3	6.8	7.1
Turbidity (NTU)	3	1	1.2
Total Suspended Solids (mg/L)	6.1	1.8	2.9
Soluble P (mg/L)	3.6	1.4	5.6
COD (mg O ₂ /L)	27	27	20.7
Total N (mg/L)	-- ^a	3.7	8.8

^a Data not available

Table 2

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

LDHs	LDHs synthesized at		Calcined
	60°C	450°C	LDHs
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-Fe(Cl)	13.8 ± 0.4	--	20.3 ± 0.6
Ca ₁ Mg ₁ -Al(NO ₃)	85.9 ± 2.9	42.7 ± 1.3	--
Ca ₁ Mg 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	--
Ca _{1.5} Mg _{0.5} -Al(NO ₃)	97.9 ± 0.5	96.8 ± 0.4	--
Ca _{1.5} Mg _{0.5} -Fe(NO ₃)	97.1 ± 0.7	98.3 ± 0.2	--
Ca _{1.5} Mg _{0.5} -Fe(Cl)(NO ₃)	85.8 ± 1.6	--	84.5 ± 1.8

SD = standard deviation (n = 3), ^a Data not available

Table 3

Variation of element in the CaAl(NO₃)-60 LDH before and after phosphate uptake.

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	8.30
Total (%)	100	100

Table 4

Analysis of ions in the supernatant

Sample	Concentration of ions in mg/L (with ion release percentage in parenthesis)						Loss of total ions (%)
	Ca ²⁺	Mg ²⁺	Fe ³⁺	Al ³⁺	NO ₃ ⁻	Cl ⁻	
Ca-Al(NO ₃)-60	28.4 (9.5)	-	-	8.1 (2.7)	107.2 (35.7)	-	47.9
Ca-Al(NO ₃)-450	30.2 (10.1)	-	-	8.4 (2.8)	120.5 (40.2)	-	53.1
Ca-Fe(Cl)-60	27.9 (9.3)	-	0.1 (0.1)	-	-	67.2 (22.4)	31.8
Ca-Fe(Cl)-450	34.9 (11.6)	-	0.0 (0.0)	-	-	79.2 (26.4)	38
Mg-Fe(NO ₃)-60	-	14.7 (0.7)	0.0 (0.0)	-	-	391.0 (19.6)	20.3
Mg-Fe(Cl)-60	-	23.8 (1.2)	0.0 (0.0)	-	-	79.1 (3.9)	5.1
Mg-Fe(Cl)-450	-	18.2 (0.9)	3.7 (0.2)	-	-	72.0 (3.6)	4.7
Ca _{1.5} Mg _{0.5} -Fe(NO ₃)-60	21.7 (7.2)	2.3 (0.8)	0.1 (0.1)	-	86.4 (28.8)	-	36.9
Ca _{1.5} Mg _{0.5} -Al(NO ₃)-60	20.1 (6.7)	1.6 (0.5)	-	7.1 (2.4)	85.5 (28.5)	-	38.1
Ca _{1.5} Mg _{0.5} -Fe(Cl)(NO ₃)-60	27.3 (5.5)	0.0 (0.0)	0.0 (0.0)	-	15.5 (3.1)	71.9 (14.4)	23
Ca _{1.5} Mg _{0.5} -Fe(Cl)(NO ₃)-450	24.6 (4.9)	0.0 (0.0)	0.0 (0.0)	-	5.1 (1.0)	86.4 (17.3)	23.2

Table 5

Analysis of ions in the supernatant after adsorption-desorption operation.

Ion	Concentration of ions in mg/L (with ion release percentage in parenthesis)		
	Sorption run-1	Desorption run-1	Sorption run-2
Ca ²⁺	43.3 (8.7)	31.4 (7.3)	8.8 (1.7)
Mg ²⁺	0.0	3.8 (0.9)	0.0
Fe ³⁺	0.0	9.7 (2.2)	0.0
Cl ⁻	90.5 (18.1)	67.7 (15.6)	0.5 (0.1)
NO ₃ ⁻	5.0 (1.0)	7.1 (1.6)	0.0