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# Strategic phosphate removal/recovery by a re-usable Mg-Fe-Cl layered double hydroxide

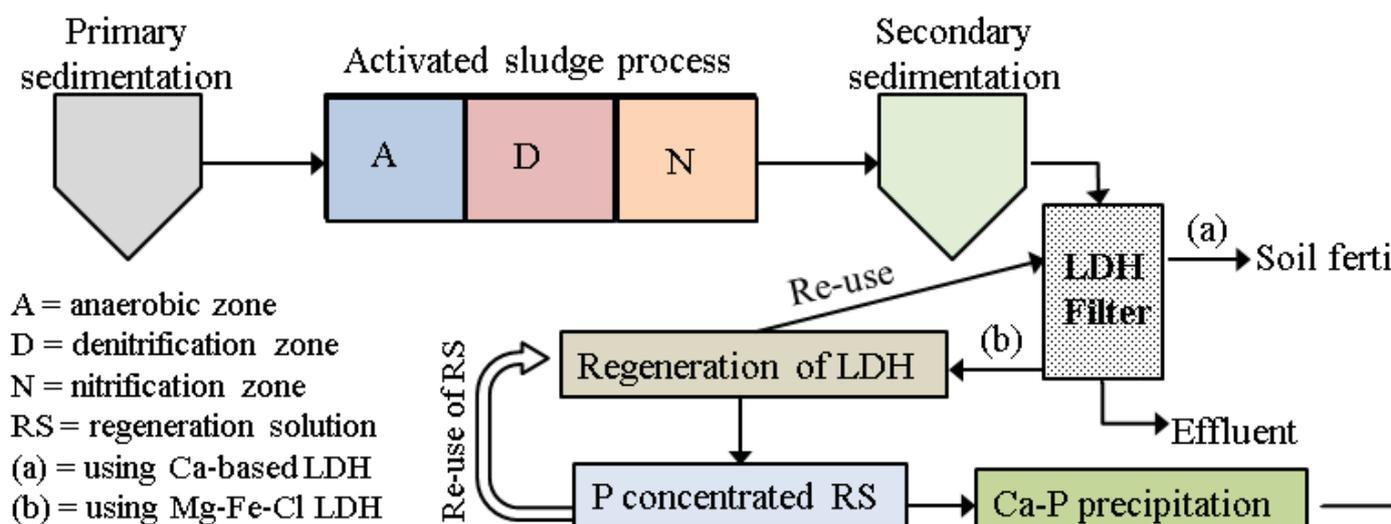
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Graphical Abstract



Highlights

- Mg-Fe-Cl based layered double hydroxides (LDHs) were prepared for removing phosphate (P).
- Mg-Fe-Cl LDH can reduce phosphate concentration down to 0.1 mg/L at equilibrium.
- Mg-Fe-Cl LDHs have stable structure and can be regenerated and reused at least for 6 cycles.
- Ligand exchange by OH<sup>-</sup> ions and anion exchange with Cl<sup>-</sup> contribute to the phosphate removal.
- LDHs can be implemented as a tertiary wastewater treatment to meet stringent P discharge regulations.

**ABSTRACT**

Excess phosphorus (P) in freshwater bodies is one of the major causes of eutrophication. The regulations for removing phosphate from wastewater treatment plant (WWTP) are becoming more

stringent and thus the alternative technologies are sought to enhance the P removal efficiency. In this study, Mg-Fe-Cl based layered double hydroxide (LDH) compounds were synthesized and used for phosphate removal. Implementing LDH as a tertiary treatment process for the removal and recovery of phosphate is proposed. Results show that LDH dosage of 2 g/l can reduce phosphate concentration down to 0.1 mg/l from an initial value of 10 mg/l at an equilibrium contact time of 2 and 3 h, respectively. The adsorption kinetics of phosphate onto Mg-Fe-Cl LDH is well governed by the pseudo-second-order kinetic model, and adsorption data fit well to the Langmuir and Freundlich isotherms. The study on pH effect of adsorbate solution suggested that pH range between 3–7.5 is suitable for unaffected phosphate removal. The repeated use of this LDH by both batch and fixed bed column experiment showed that total phosphate reduction was about 95% and desorption percentage was about 91% through six cycles of adsorption-desorption processes. It is likely that this LDH compounds can be applied to remove and recover phosphate from secondary effluent of domestic wastewater treatment plant and thereby, to meet future stringent discharge regulations.

**Keywords** : Layered double hydroxide; phosphate removal; sorption; desorption; re-use.

## 1. Introduction

Excess phosphorus (P), even at minimal amount for example  $>0.1$  mg/l, in freshwater bodies (e.g. lakes, rivers) is one of the major causes of eutrophication (known as the process to extensive growth of water plants, algae, and plankton), resulting ecological unbalance (Xu et al., 2010). In the UK, 80% of 98 surveyed rivers were found to exceed the accepted standard of healthy rivers' background P concentration, e.g. 0.1 mg/l (Pratt et al., 2012). The regulations for removing phosphate from wastewater treatment plant (WWTP) are becoming more stringent (e.g. P concentration in WWTPs' effluent is targeted to be limited to 0.01 mg/l by 2027 in the USA (You et al., 2016)). The European Union (EU) also considers that lakes with total P concentration  $<0.01$

mg/l is not at risk of eutrophication, whereas, those with  $>0.1$  mg-P/l is at risk, and rivers with total P concentration less than 0.01–0.07 mg/l is considered excellent waters (European Commission, 2009). Thermodynamic and kinetic limitations of conventional treatment constrain biological P removal and precipitation-sorption processes to about 0.1 mg/l in final effluent (Mayer et al., 2013). Moreover, chemical precipitation is associated with excessive sludge production, high operating costs, and problems of disposing P-rich sludge without further chemical treatment (de-Bashan and Bashan, 2004; Parsons and Smith, 2008). P is becoming more constrained with a measurable worldwide depletion of phosphate mineral reserves. Natural P stocks are predicted to be depleted by 2050, or within the next 50 years. This is a major concern (Gilbert, 2009; Zhou et al., 2012) because P is a known non-renewable resource that is critical for life supporting biochemical processes as well as a component in consumer goods such as detergents, fertilizers, water softeners and processed foods. So, there is an emerging demand to not only removing P from wastewater but also to recover it as secondary P resources (e.g. P-loaded minerals).

In recent years, a number of isostructural layered double hydroxide (LDH) based inorganic adsorbents have been investigated to remove oxyanion contaminants (e.g. arsenite, arsenate, borate, chromate and selenate) from water (Jiang et al., 2007; Cheng et al., 2010; Zhou et al., 2011; Guo et al., 2012; Theiss et al., 2014). LDHs are a class of two-dimensional nanostructured anionic clays (e.g. average particle size of Mg-Al-LDH was reported to be  $<100$  nm) (Jiang et al., 2007), and their main structure consists of positively charged brucite-like ( $\text{Mg}(\text{OH})_2$ ) sheets and a negatively charged interlayer regions 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. Thus, LDHs possess good anion exchange property. Also, the removal mechanism of anions by LDHs has been reported to be due to surface adsorption by forming inner sphere complex through ligand exchange with  $\text{OH}^-$ , surface

precipitation, and intercalation by reconstruction of the calcined LDH structure (Turk et al., 2009; Loganathan et al., 2014). Based on the general formula of LDH structure ( $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ ; where  $M^{2+}$  and  $M^{3+}$  denote divalent and trivalent cations, respectively,  $A^{n-}$  is the interlayer anion of valence  $n$ , and  $x$  is equal to the molar ratio of  $M^{3+}/(M^{2+} + M^{3+})$  typically ranges from 0.18 to 0.33), various metal precursor i.e. cation pairs (e.g. Mg-Al, Mg-Fe, Zn-Al, Zn-Cr, Ca-Al, Ca-Fe, Mg-Ca-Fe, Mg-Ca-Al) and intercalated anions (e.g.  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ) can be incorporated into LDH layers through different synthesis techniques, including co-precipitation method, modified co-precipitation involving separate nucleation and ageing steps, hydrolysis method, ion-exchange process and hydrothermal method (e.g., Goh et al., 2008). Among these, Mg-Al, Mg-Fe, Ca-Al and Ca-Fe LDHs with  $CO_3^{2-}$  or  $Cl^-$  as the interlayer anion, and co-precipitation as the synthesis technique are the most common; and these LDHs have been demonstrated to remove oxyanions like phosphate, arsenate, arsenite, etc. from aqueous phase in several studies (Xing et al., 2008; Chitrakar et al., 2010; Caporale et al., 2013; Tsuji and Fuji, 2014). Although Mg-Al and Mg-Fe LDHs were applied to remove phosphate from water in some previous studies (Das et al., 2006; Chitrakar et al., 2010), very few of them considered re-usability of the material. Moreover, most of the investigations were conducted under batch sorption process which is not suitable for application under a real case scenario in wastewater treatment plants e.g. treating secondary effluent. It is pertinent to know the continuous adsorption data which can be achieved through empty bed column experiments.

In the present study, Mg-Fe-Cl LDH was prepared following co-precipitation method and applied to assess the phosphate removal under both batch and column study modes. The potential of the regeneration and re-use of this sorbent material was also investigated.

## **2. Materials and methods**

### ***2.1. Preparation and characterization of Mg-Fe-Cl LDH***

The LDH materials were prepared by the coprecipitation method and followed a procedure shown in Fig. S1. The resulting dried LDHs were repeatedly washed with deionized water to free excess  $\text{Cl}^-$  ions. Finally, the wet LDH solid was dried at  $60^\circ\text{C}$  for 24 h, and gently crushed and sieved to the fraction of 0.3–0.7 mm. Some portion of the LDHs obtained in this way was also calcined at  $450^\circ\text{C}$  for 2 h.

LDH samples were characterized physicochemically before and after phosphate adsorption. Phosphorus-loaded LDH (P-LDH) was obtained via the removal of phosphate from adsorbate solution, followed by washing with deionised water, and drying at  $60^\circ\text{C}$  for 20 h. The structural patterns of the LDH samples were characterized by X-ray diffraction (XRD) analyses using a Siemens D5000 Diffractometer, employing  $\text{Cu K}_\alpha$  radiation with a step size of  $0.02^\circ$  and a counting time of 1s per step. The measurements were run in the  $2\theta$  range of  $5\text{--}85^\circ$ , and samples were prepared by compaction into a silicon sample holder. A Fourier transform infrared spectroscopy (FTIR, Jasco FT/IR-6100) was used to determine the presence of functional groups in the samples. The morphology of the LDH samples was examined by scanning electron microscopy (SEM, Carl Zeiss EVO50 XVP) equipped with energy dispersive X-ray (EDX) facility (Oxford Instruments X-Max, Resolution 129 eV).

The composition of the synthesized LDH product was determined using the mass balance protocol. In this case, following the centrifugation step in the synthesis process, the supernatant was collected by separating from solid precipitates via filtration and measured to record the volume. Finally, the mass difference between the ions dosed in the preparation step and the ion residuals in the supernatant was used to determine the ion content in the LDH product (Jiang et al., 2007). The concentration of various ions (e.g.  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cl}^-$ ) in the aqueous phase was determined using a RFID enabled HACH DR3900 spectrophotometer using respective calibrants supplied by HACH Lange, UK.

## **2.2. Adsorbate solution**

The working adsorbate solution with the desired P concentration for batch sorption and column studies was freshly taken from the phosphate stock solution of 50 mg P/l, which was prepared by dissolving AR grade  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  into deionized water. The pH of the working solutions was adjusted manually to the required values by diluted NaOH or HCl solutions.

Domestic sewage effluent after secondary settlement process was collected from Shieldhall Waste Water Treatment Works (WWTW) at Glasgow, Scotland (UK) for treating with selected LDH.

## **2.3. Batch experiments**

Phosphate sorption experiments were conducted as a function of LDH dosage, contact time, initial pH of solution and initial adsorbate concentration. Also, desorption of phosphate and re-usability of LDH compound were assessed under batch study mode.

Adsorption studies: All batch sorption experiments were performed in duplicate at room temperature using 50 ml polypropylene conical tubes. Various amounts (12.5–50 mg) of LDH compound were introduced into 25 ml of adsorbate solution with an initial total P concentration of 10 mg/l and a pH  $\sim 7$ . The mixing of LDH and adsorbate solution was performed by using an orbital shaker (MAXQ 4450, Thermo Scientific) at 250 rpm for 24 h. After shaking, the suspension was immediately centrifuged for phase separation and the supernatant pH was measured. The supernatant was collected through filtration by using syringe filter (0.45  $\mu\text{m}$  Whatman filter disc), and analysed to determine the residual P concentration. The LDH dosage was determined by applying the method to a range of sorption runs. Then, to determine equilibrium contact time, the time-dependent sorption of phosphate was carried out at selected time intervals between 0.25 to 6 h while the initial P concentration, LDH dosage and solution pH were fixed at 10 mg/l, 2 g/l and  $\sim 7$ , respectively. P sorption was measured under different initial P concentrations (5–40 mg/l) and

at various initial pH levels (3–11) to determine the adsorption isotherms and the effect of pH, respectively. The shaking time applied was 2 h for determining both the isotherm equilibrium and pH effect. All other procedures applied remained aligned to the methodology described for the adsorption experiments. The results are presented as the average of duplicate trials, and the reproducibility of the results were varied within the standard deviation  $\leq \pm 5\%$ . The adsorption capacity ( $Q_e$ , mg/g) or quantity 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).

Desorption studies: Calcined Mg-Fe-Cl LDH was studied in the subsequent phosphate sorption-desorption cycles. In the first cycle, phosphate sorption was conducted for 20 h at room temperature by adding LDH (2 g/l) to the adsorbate solution (10 mg-P/l, pH =7.0). Phosphate saturated LDH (P-LDH) was then separated by centrifugation and the supernatant was withdrawn to determine residual phosphate concentration. Then, the solid phase of P-LDH was washed in deionized water to remove any unadsorbed phosphate, and subsequently mixed with different concentrations of alkaline desorbing solution (1–8% of NaOH) to evaluate phosphate desorption. The desorption shaking was run for 20 h using the estimated volume of selected desorbing solution required to maintain a solid to liquid ratio of 2 g/l. The mixture was then centrifuged and the supernatant was analyzed to measure the extent of phosphate release. After desorption run, the resulting LDH solids were separated, washed by deionized water several times and then, regenerated by calcination at 450°C for 2 h. In this way, the LDH was regenerated and reused up

to 6 cycles, and phosphate contained desorbing solution was re-used in the following desorption cycles.

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

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

where  $C_o$  is the initial concentration of P (mg/l);  $C_{(i)}$  is residual concentration of P in the  $i$ th adsorption operation (mg/l);  $Q_{ads(i)}$  is amount of P uptake in the  $i$ th adsorption operation (mg-P/g LDH);  $Q_{des(i)}$  is the amount of P released in the  $i$ th desorption operation (mg-P/g LDH).

#### **2.4. Laboratory column experiments**

Continuous sorption studies were conducted by using Mg-Fe-Cl LDH packed column in order to evaluate the applicability of LDH material to remove phosphate on an industrial scale e.g. under a continuously generated secondary effluent in wastewater treatment plants. Both P-spiked test solutions and secondary effluent from domestic WWTW were used in these studies. The re-usability of the exhausted LDH was also investigated in continuous sorption-desorption cycles.

Set-up of column filtration: Two different sizes of glass columns with heights of 20, 25 cm and inner diameters of 1.1, 1.4 cm, respectively, were packed by Mg-Fe-Cl LDH up to the bed depth of 1.1 and 2.2 cm, respectively. The corresponding sorbent bed volumes were calculated as 1.045 and 3.387 ml, respectively. Glass wool was used at the bottom of the packed bed depth to avoid any loss of the LDH particles. Then, phosphate test solution ([P]=2 mg/l, pH=7.0) was introduced downward at the flow rate of 1.5 and 5 ml/min, respectively, to the packed column with bed volume of 1.045 ml, and at 10 ml/min to the one with 3.387 ml bed volume by a peristaltic pump (Sci 400/120S, Watson Marlow). Treated effluent samples were collected at various time intervals and were analyzed to determine the residual P concentration. The inflow was continued until the effluent P concentration ( $C$ ) approximately reached about 1 mg/l, i.e. up to 50% of the

initial concentration ( $C_0$ ). Similarly, secondary effluent of WWTW was also assessed for P removal using the LDH packed column with bed volume of 1.045 ml and at flow rate of 5 ml/min.

Sorption/desorption column study: After first sorption cycle, deionized water was initially pumped through the packed column for 3.33 h at 5 ml/min and then, selected desorbing solution (2% NaOH) was flowed through the column. The extent of P release was analysed. Finally, before commencing the next sorption cycle, the column was washed with 500 ml of deionized water at the same flow rate. In this way, the sorption cycles were repeated five times without any further modifications of the used LDH. However, from second desorption run 4% NaOH was used in the subsequent cycles.

### ***2.5. Analytical approach and data analysis***

All the pH measurements were carried out with a pH meter (Cyberscan pH 11, Eutech Instruments) and the accuracy of pH reading was checked time to time using buffer solutions with pH of 4.0 and 7.0. 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 with a spectrophotometer (DR3900, HACH) at absorbance 880 nm by following the ascorbic acid method (APHA, 2005).

The batch study data from time-dependent sorption experiment were analysed by two mathematical models: pseudo first-order ( $\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$ ) and pseudo second-order ( $\frac{t}{q_t} = \frac{1}{k_2 b q_e^2} + \frac{t}{q_e}$ ) models, where  $q_e$  and  $q_t$  (mg/g) are the amount of P adsorbed on the adsorbents at equilibrium and at time  $t$  (h);  $k_1$  (1/h) and  $k_2$  (g/mg h) are the rate constants of first-order and pseudo second-order kinetic models.

Also, batch sorption data obtained from using different levels of initial P concentration were analysed using the linear forms of Langmuir ( $\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0}$ ) and Freundlich ( $\log q_e = \log K_f + \frac{1}{n} \log C_e$ ) isotherm models; where  $q_0$  = 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.

Column study data were assessed by calculating the numbers of treated bed volume (BV) and empty bed contact time (EBCT) as follows:

$$BV = \frac{\text{volume of the treated effluent (ml)}}{\text{volume of the adsorbent bed (ml)}}, \quad EBCT = \frac{\text{volume of the adsorbent bed (ml)}}{\text{flow rate (ml/min)}}$$

### 3. Results and discussion

#### 3.1. Physicochemical characteristics of LDH samples

The formation of LDH structure in the prepared Mg-Fe-Cl-60 samples is confirmed by the XRD analysis. As seen from Fig. S2 (i-a), the XRD patterns of the as-synthesized Mg-Fe-Cl-60 sample is typical of a LDH phase with sharp and characteristic reflections corresponding to the (003), (006), (110) and (113) planes; and broad peaks from the (009), (015) and (018) planes. According to the Inorganic Crystal Structure database (ICSD), these are characteristic planes of hydroxyl-like compounds and they match well with the expected reference pattern of ICSD 81963 (Goh et al., 2010; Kang et al., 2013). The characteristic presence of surface hydroxyl groups and interlayer water molecules are confirmed from the FTIR spectra of the synthesized Mg-Fe-Cl-60 LDH (Fig. S2 (ii)). The strong and broad band at about 3300–3420  $\text{cm}^{-1}$  is associated with a superposition of hydroxyl stretching band arising from metal-hydroxyl groups (MO-H) in the layers and hydrogen-bonded interlayer water molecules. The band at 1628  $\text{cm}^{-1}$  represents H-O-H deformation, indicating the presence of interlayer water molecules.

After reaction with phosphate solution, Mg-Fe-Cl-60 LDH showed an enlargement of the basal spacing ( $d_{003}$ ,  $d_{006}$ ) with corresponding less sharp reflections by the basal (00 $l$ ) planes compared to the pristine (Fig. S2 (i-a, b)). This is in conformity with the fact that phosphate anions intercalated into the Mg-Fe-Cl-60 LDH and consistent to other reported observations (Novillo et al., 2014).

The effect of calcination at 450°C is visible from both XRD and FTIR analysis of Mg-Fe-Cl-450 LDH (Fig. S2 (i-c, ii)), where XRD pattern shows that the peaks of hydroxylated structure are absent due to the collapse of layered phase and FTIR spectra reveals the removal of interlayer water and anions; resulting the formation of intermediate non-stoichiometric metal oxides (e.g.  $Mg_xFe_xO$ ). After being contact with phosphate solution, calcined Mg-Fe-Cl-450 samples were expected to regain the LDH type structure through rehydration and sorption of phosphate anions, which is somewhat reflected in the XRD peaks of P-loaded Mg-Fe-Cl-450 LDH (Fig. S2 (i-d)), however, some typical reflections corresponding to the (003) (006) and (009) planes are not clearly present.

SEM images of LDH samples (before and after P sorption) can be viewed in Fig. S3, which shows the aggregation of particles in different shapes of plate-like well-developed layered structure. The analysis of EDX spectrum confirms the presence of magnesium (Mg), iron (Fe), oxygen (O), sodium (Na) and chloride (Cl) in the as-synthesized Mg-Fe-Cl LDH samples (Table 1). The mass balance results (following a similar method of a previous study by Jiang et al., (2007) shown in Table 2 suggest that the composition of the Mg-Fe-Cl LDH is roughly in accordance with the molar ratio of Mg to Fe (2:1) applied in the synthesis process, but the content of Cl and Na in the pristine solid is highly reduced due to several washing steps in the preparation process. The elemental composition (based on Table 1) of the pristine solid also supports the proposed chemical formula for Mg-Fe-Cl LDH, when the results of the elemental analysis are fitted into the formula of LDH phase  $[Mg_xFe_y(OH)_{2(x+y)}](Cl)_y(H_2O)_n$ . Accordingly, the chemical formula can be estimated as  $Mg_{2.05}Fe(OH)_{6.1}Cl_{0.3} \cdot 0.2H_2O \cdot 0.263NaCl$ . However, the electronic balance is absent in this formula as evident from the higher positive charges ( $2 \times 2.05 + 3 \times 1 = 7.1$ ) than the negative one ( $1 \times 6.1 + 1 \times 0.3 = 6.4$ ), which implies that 0.35 mol carbonate ( $CO_3^{2-}$ ) ions could be present in the interlayer to contribute to the electronic balance of the proposed LDH formula. The source of

carbonate perhaps came from the atmospheric air during the preparation of LDH materials; the same phenomenon was observed by Violante et al., (2009).

Given the above Mg-Fe-Cl LDH formula,  $\text{Mg}_{2.05}\text{Fe}(\text{OH})_{6.1}\text{Cl}_{0.3}\cdot 0.2\text{H}_2\text{O}\cdot 0.263\text{NaCl}$ , the proposed Mg-Fe-Cl LDH contains two types of Cl ions which can be exchanged by phosphate ions; 1.17 mmol in LDH compound and 1.0 mmol in occluded NaCl.

After phosphate sorption, it can be seen from Fig. S3 (b, d) that the crystalline plate-like layered structure still remains and there was small loss of Mg and Na (Table 1), which demonstrates the mineral stability of the samples. Moreover, decreasing in contents of chlorine with increasing in phosphorus in the used LDH (Table 1) indicates that anion exchanges between  $\text{Cl}^-$  and phosphate anions took place, and this adsorption of phosphate also corresponded well with the increase in O content.

### ***3.2. Phosphate uptake by Mg-Fe-Cl LDH in batch study***

Effect of dosage: The effect of LDH adsorbent's dosage on phosphate removal is shown in Fig. 1a. The removal efficiency reached to a level of >99% at dosage starting from 1.5 g/l for both Mg-Fe-Cl-60 and calcined Mg-Fe-Cl-450 LDHs. For LDH dosage of 2 g/l, the measured removal of phosphate was about 99.7% from 10 mg-P/l solution with corresponding sorption capacity of about 5 mg-P/g LDH.

Effect of contact time and kinetic studies: Phosphate removal increased swiftly with increasing contact time starting from 15 min to 60 min, which then started to level off beyond 2 h (Fig. 1b). The equilibrium time required to remove about 99% phosphate was 2 and 3 h, respectively, for Mg-Fe-Cl-450 and Mg-Fe-Cl-60 LDHs. Further batch sorption experiments on the effect of pH and initial phosphate concentration were conducted with calcined Mg-Fe-Cl-450 LDH at selected dosage of 2 g/l and contact time of 2 h.

To understand the mechanism of phosphate sorption by LDHs, the time dependent sorption data were fitted to pseudo-first-order and pseudo-second-order kinetic models. From Table 3, it can be seen that the correlation coefficients  $R^2$  of pseudo-second-order model are higher than those of pseudo-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 Mg-Fe-Cl LDHs is well governed by the pseudo-second-order model, suggesting that chemisorption process (bond formation at LDH's surface) was occurred for phosphate uptake. Previous studies (e.g. Novillo et al., 2014) on phosphate removal by Mg/Al-LDHs have also reported the similar phenomena of the adsorption kinetics.

Effect of initial phosphate concentration and adsorption isotherm: The uptake of phosphate on Mg-Fe-Cl-450 LDH was evaluated for a range of initial P concentrations between 5 and 40 mg/l, and the results are shown in Fig. 1c. The residual P concentration was observed to be about 0.1 mg/l (i.e. 99% removal rate) for an initial concentration up to 10 mg/l. However, removal rate of phosphate decreased with further increase of initial concentration due to the lack of available active sites that can accommodate increased phosphate species at fixed adsorbent dosage.

The data were used to plot Langmuir and Freundlich isotherm model relationships, and values of isotherm constants are presented in Table 4. The values of correlation coefficients ( $R^2$ ) in Table 4 indicate the better applicability of Langmuir isotherm model to describe phosphate adsorption capacity by Mg-Fe-Cl LDH, which is consistent with other studies (Cheng et al., 2009; Cai et al., 2012) in phosphate removal by LDHs. The estimated maximum phosphate adsorption capacity on Mg-Fe-Cl-450 LDH is 9.8 mg-P/g as per Langmuir model (Table 3), which could be varied from

study to study due to various factors, such as the composition and properties of the LDHs used; the characteristics of co-existing anions in the solution/water studied and the experimental approaches used. According to the Cl anions content in the Mg-Fe-Cl LDH-450 (Table 1), the theoretical P up-taking capacity of this formula LDH can be estimated as 14.89 mg-P/g, when anion exchange is considered to be the only removal process. The fitness of the Langmuir isotherm to predict phosphate affinity by Mg-Fe-Cl LDH can also be assessed using the Langmuir parameter  $b$  and initial phosphate concentration ( $C_0$ ) to obtain the separation factor  $R_L$  ( $R_L = 1/(1+bC_0)$ ) (Jiang et al. 2007). When  $0 < R_L < 1$ , the adsorption system is favourable. In the current study, the values of  $R_L$  were found to be in the range of 0.002 to 0.014 with a decreased separation factor at high phosphate concentrations, which indicates a highly favourable adsorption of phosphate on Mg-Fe-Cl LDH.

Effect of solution pH: The effect of different initial pH values ranging from 3 to 11 on the sorption of phosphate onto Mg-Fe-Cl-450 LDH is shown in Fig. 1d. The removal rate was almost steady (~98.9%) in the pH range between 3–7.5; however, with further increase in pH up to 11.0, there was a steady decrease. The species distribution of phosphate in aqueous solution is pH related at different acid dissociation constants ( $K_a$ ) according to Eq. 1 (Cheng et al., 2009):



In the pH range between 3 and 11,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  were the dominant species, where the monovalent ( $\text{H}_2\text{PO}_4^-$ ) ions were easily adsorbed at pH 3–7.5 by ion exchange with interlayer  $\text{Cl}^-$  ions of the LDH. The decrease of phosphate adsorption with increasing solution pH is reasonable because of the fact that higher pH causes increasing competition for adsorption sites between  $\text{OH}^-$

groups and phosphate species (e.g. mainly  $\text{HPO}_4^{2-}$  at  $\text{pH} > 7.5$ ). Moreover, the equilibrium pH was observed to be raised to 9.9 after sorption for initial solution pH range 3–7.5 (Fig. 1d), which indicates a strong buffering capacity of Mg-Fe-Cl LDH with no significant changes in removal rate for this initial pH range. Due to such phenomena, ligand exchange interaction between hydroxyl groups of the LDH surface (M-OH) and anionic phosphate species can also be proposed as the removal process of phosphate by the LDH.

Desorption and regeneration: Preliminary trials were conducted to select appropriate desorbing solution using different concentrations of NaOH under different contact time and the results are shown in Fig. S4a. It was observed that desorption rate of phosphate was increased sharply with the increase of concentration of NaOH up to 4% under contact time between 1–22 h. Further increase in desorption rate against the use of higher concentration of NaOH beyond 4% was almost insignificant when contact time was more than 2 h. Since the use of 4% NaOH (i.e. 1 mol-NaOH/l) at contact time of 22 h was adequate to achieve about 99% desorption rate, this was used as desorbing solution in the following desorption-regeneration studies.

The performance of calcined Mg-Fe-Cl LDH for phosphate removal in repeated cycles of sorption-desorption is shown in Fig. S4-b. While the maximum removal efficiency (i.e. sorption rate) of about 99% was noticed with freshly prepared LDH, however, the removal efficiency fluctuated between 86–98% in the consecutive regeneration cycles with a decreased trend from 4<sup>th</sup> cycle. The sorption capacity was decreased by 14% after 6 cycles of sorption run in comparison to that of pristine LDH (from about 5 to 4.3 mg-P/g of LDH). The accumulated adsorbed amount of phosphate after 6 cycles was about 18.1 mg-P/g of LDH, which was about 95% of the total phosphate initially dosed into the system. The desorption rate remained above 95% throughout 6 cycles, resulting a P enriched desorbing solution with about 91% recovered P from the total input. Moreover, analysis of ions in the supernatant of desorbing solution after first desorption run

showed the presence of very low concentration of Mg (8.5 mg/l) and Fe (0.2 mg/l) corresponding to only 0.5 and 0.2% dissolution, respectively, and thus indicating a relatively high chemical stability of Mg-Fe-LDH in a highly alkaline medium of 4% NaOH solution. Drenkova-Tuhtan et al., (2013) also observed negligible dissolution of MgFe-Zr LDH when applied for multiple cycles of desorption run using a highly alkaline medium (pH 12.9) with the detected concentrations of Mg and Fe at 2 and 0.9 mg/l, respectively. They had conducted 15 adsorption/desorption cycles and observed the adsorption and recovery efficiency of 88 and 83.5%, respectively, against the total input phosphate with about 20% reduction of sorption efficiency after 15 cycles. In contrary, Cheng et al., (2009) observed elevated levels of metal cations (e.g. 85 mg-Zn/l, 36.1 mg-Al/l) in the desorbing solution (consist of 5% NaOH) while using Zn-Al LDH for phosphate recovery from sewage sludge filtrate. In this case, they found about 40% less phosphate uptake after 6 cycles compared to that of pristine LDH.

### ***3.3. Column study analysis***

The breakthrough profiles of phosphate by Mg-Fe-Cl LDH filled column in a continuous-mode operation with solution containing 2 mg-P/L at pH about 7 under different empty bed contact time (EBCT) is shown in Fig. 2a. The results clearly indicate that the number of treated bed volumes (BV) increase with the increase of EBCT for the same influent concentration. For example, the breakthrough occurred at 4075, 2481 and 1626 BV, respectively, for EBCT of 0.7, 0.34 and 0.21 min when final concentration reached from 2 to 0.1 mg-P/l i.e. at  $C/C_0$  value of 0.05. This could be related to the fact that higher EBCT causes the diffusion process between LDH filter bed and P solution more effective (e.g. longer reaction time for phosphate to be adsorbed by LDH particles), resulting higher sorption capacity for phosphate. These findings correspond well with the observation by other researchers (Dong et al., 2009; Xu et al., 2011; Sun et al., 2014). The treated

BV reached up to 11594, 10625 and 8227 (ml/ml), respectively, in the order of EBCT 0.7>0.34>0.21 min when the column filter bed was about 50% saturated with adsorbed phosphate. The cumulative adsorbed amount of phosphate on Mg-Fe-Cl LDH can be estimated from the breakthrough profile as shown in Fig. 2b. As seen from this figure, sorption capacity increased with the increase of residual P concentration upon continued inflow, with an initial sharp rise irrespective of EBCT. When residual P concentration reached to 1 mg/l, the corresponding sorption capacities were 10.9, 9 and 7.5 mg-P/g LDH, respectively, for EBCT of 0.7, 0.34 and 0.21 min. So, the selection of EBCT on designing fixed-bed column is an important factor in order to achieve the optimal sorption capacity or treatment performance. Moreover, based on the use of three different flow rates, the surface loading rate (SLR), where SLR is a hydraulic loading factor expressed in terms of flow per surface area, can be correlated with the effluent treatment capacity as shown in Fig. 3. The correlation of treatment capacity and SLR in Fig. 3 shows that both target P discharge concentration and column design parameters (e.g. flow rate, bed volume) will determine the treated volume of effluent. The estimated effluent treatment capacity ranged 2–4 and 5–8 m<sup>3</sup>/kg-LDH for the discharged P concentration of 0.1 and 0.5 mg/l, respectively.

The reusability of Mg-Fe-Cl LDH was also assessed by repeating column sorption-desorption run for up to 5 cycles as shown in Fig. S5, and in each cycle, column was regenerated when the residual P concentration reached to 1 mg/l from starting value of 2 mg/l. After first sorption run, the desorption of P by deionized water was observed to be only 1.5%, which reveals that physical bonding in the sorption of phosphate onto Mg-Fe-Cl LDH is negligible. However, the flow of 2% NaOH was able to release about 83% of the adsorbed P in 240 min at flow rate of 5 ml/min (Fig. S5a). In comparison, about 88% desorption was obtained in 90 min when 4% NaOH was used from

second cycle of regeneration. In both cases, the desorption was quick in the beginning of operation and gradually decreased with the increase of desorption time. For example, the peaks of phosphate concentrations were in the range 20–143.5 mg/l and 20–414 mg/l in desorption solutions within 10 min for 2 and 4% NaOH desorbing agents, respectively (Fig. S5a). For further desorption run, 4% NaOH was used and the subsequent desorption efficiency remained above 95%, where nearly 16–20-fold preconcentration of phosphate was achieved. The treated BV from the third cycle run was observed to be between 5511–5598 ml/ml, which was 84–85% of the one observed at second sorption run (Fig. S5b). However, the treated BV was decreased from 8226.8 to 6576.7 ml/ml (about 20% reduction) in the second cycle, which could be due to the fact that least desorption rate was occurred by using 2% NaOH in the first cycle. This indicates that either incomplete desorption or irreversible sorption could highly affect the regeneration of the LDH particles as well as further sorption performance.

### ***3.4. Treatment of secondary effluent***

Secondary effluent from wastewater treatment plant was used to assess P removal by Mg-Fe-Cl-LDH under both batch and column study process. It was observed that phosphate removal increased with LDH doses, and above 98% removal was achieved from dose of 4 g/L (Fig. 4). This indicates that at least 2-fold higher dose was required to attain the similar phosphate removal efficiency as that from the test solution (Fig. 1a). Other pollutants, total nitrogen (TN) and colour, were 30–60% removed if increasing LDH dose above 2 g/l (Fig. 4), while COD removal was lower than 10%. This explains why comparatively higher dose of LDH was required to achieve comparable P removal from real waste water effluent. The column study results showed that the treated BV was up to 3735 ml/ml when residual P concentration was reduced to 1 mg/l from 2 mg/l, which is about 45% of the BV of the treated test solution which had phosphate alone.

#### 4. Strategic requirement for phosphate removal and recovery

Effluents from waste water treatment plant are considered to contribute up to 60–80% of the P in rivers due to discharge of treated effluents often containing residual P concentrations of 1–2 mg/l (POSTnote 477, 2014). The discharge level of P from WWTPs in many countries is going to be strictly limited to 0.1 mg/l or even less due to the growing concern over eutrophication. Since conventional treatment methods mainly with biological P removal process are not capable to reduce P concentrations to or below 0.1 mg/l in the final effluent, the incorporation of adsorption based additional treatment step as a tertiary treatment method with the conventional process could be a prospective option to facilitate WWTPs to meet the future stringent P discharge limit. Moreover, there is an emerging demand to not only removing P from wastewater but also to recover it as secondary P resources (e.g. P-loaded minerals). Adsorptive removal of phosphate can thus be proposed to be a potential candidate for tertiary treatment processes in WWTPs considering the importance of future P discharge limit and its recovery.

The proposed strategy for implementing LDH based tertiary treatment process is shown in Fig. 5. Accordingly, the effluent after secondary sedimentation process can be treated with LDH based materials in a filtration unit, e.g., by using Ca-based LDH to achieve effluent P concentration of 0.1 mg/l and consequently, recovering P in the filtration unit as Ca-P solids, which can be applied for soil fertilization. If Mg-Fe-Cl-LDH is to be considered in the filtration bed media, it can be regenerated by desorption of P using 4% NaOH solution and can be re-used for P sorption. As demonstrated in this study, P can be concentrated in the desorbing solution with about 91% recovered P from the total input up to six cycles. According to several literatures (Desmidt et al.,

2015; Tolkou et al., 2015), P can be precipitated from P-rich alkaline solution using  $\text{CaCl}_2$  and recovered as Ca-P solids. The advantage of the strategy shown in Fig. 5 will be not only to meet P discharge limit but also to recover it as P-loaded minerals, which could be of significant importance for future WWTP's strategy in meeting very low P discharge limit.

## 5. Conclusion

In this study, Mg-Fe-Cl based layered double hydroxide (LDH) compounds were synthesized and used for phosphate removal. Results show that LDH dosage of 2 g/l can reduce phosphate concentration down to 0.1 mg/l from an initial value of 10 mg/l at an equilibrium contact time of 2 and 3 h for Mg-Fe-Cl-450 and Mg-Fe-Cl-60, respectively. The adsorption kinetics of phosphate onto Mg-Fe-Cl LDH is well governed by the pseudo-second-order kinetic model, and adsorption data fit well to the Langmuir and Freundlich isotherm. The removal mechanism of phosphate was predominantly due to ligand exchange by  $\text{OH}^-$  ions on the LDH surface and anion exchange with  $\text{Cl}^-$  in the interlayer region. The study on pH effect of adsorbate solution suggested that high alkaline solution ( $\text{pH} > 8$ ) decrease the phosphate removal, however, pH ranging between 3–7.5 unaffected phosphate removal. The repeated use of this LDH showed that about 95% of the total phosphate dosed into the system through six cycles was adsorbed, and about 91% of them recovered as phosphate enriched desorbing solution. Finally, both batch and fixed bed column experiment results demonstrate that this LDH compounds can be potentially applied to remove and recover phosphate from secondary effluent of domestic wastewater treatment plant and thereby contribute to achieving more demanding effluent discharge regulation, ultimately protecting the environment.

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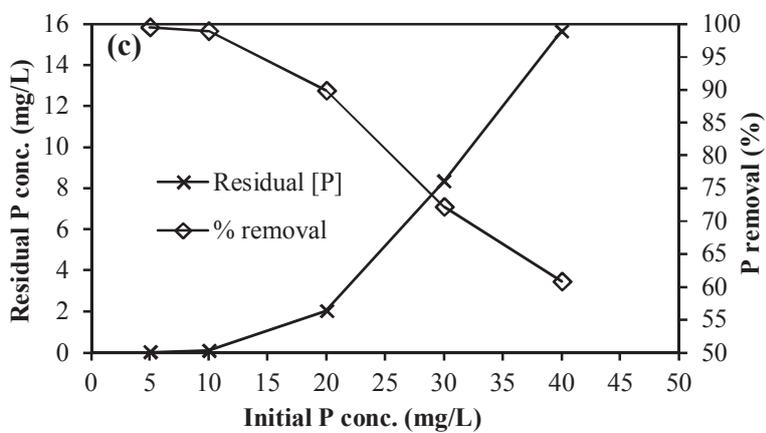
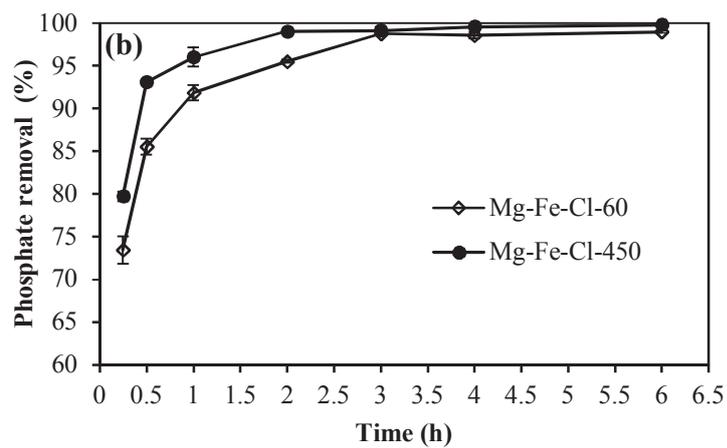
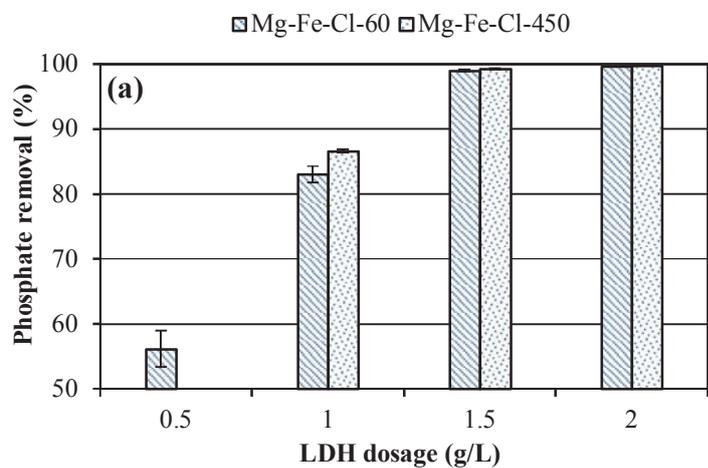
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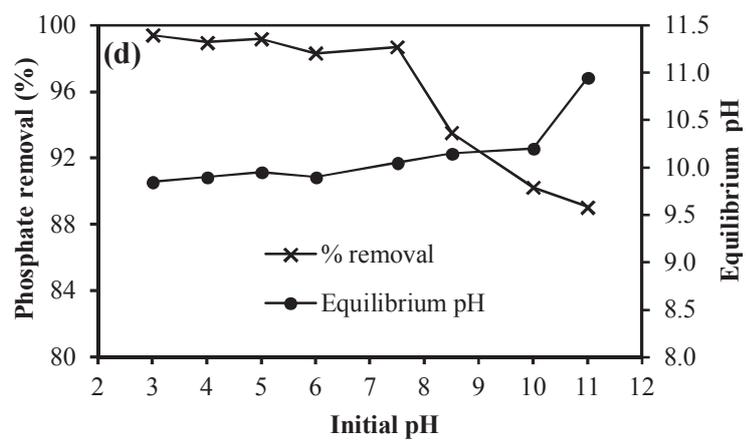
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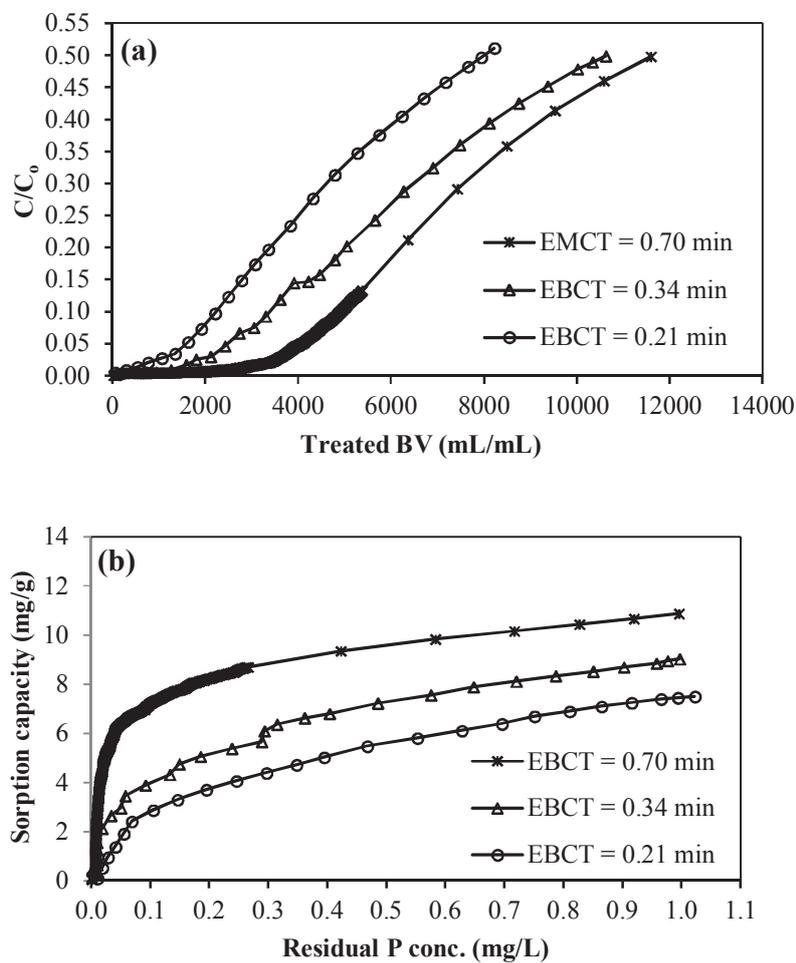
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## List of Figures

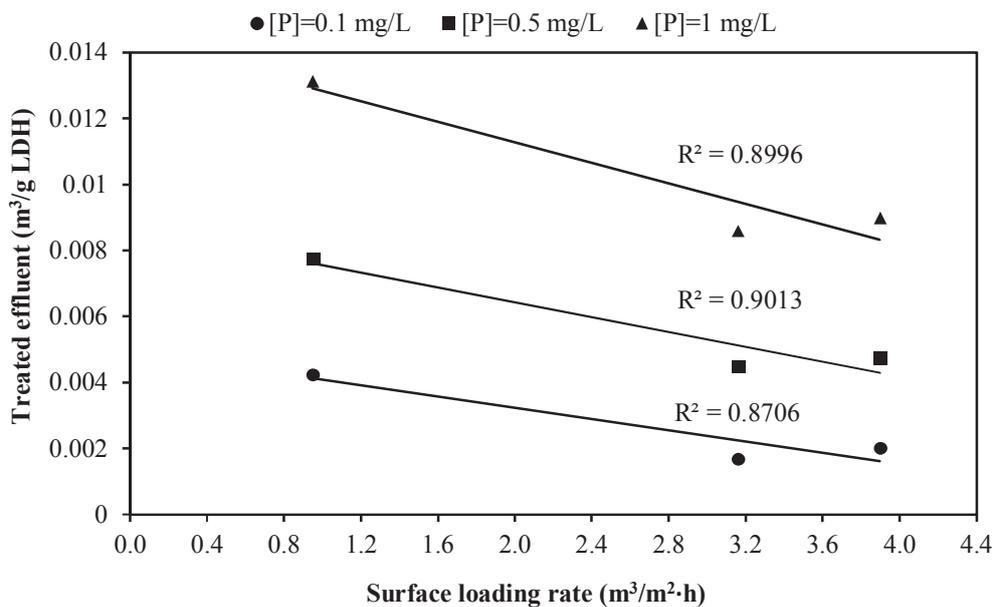




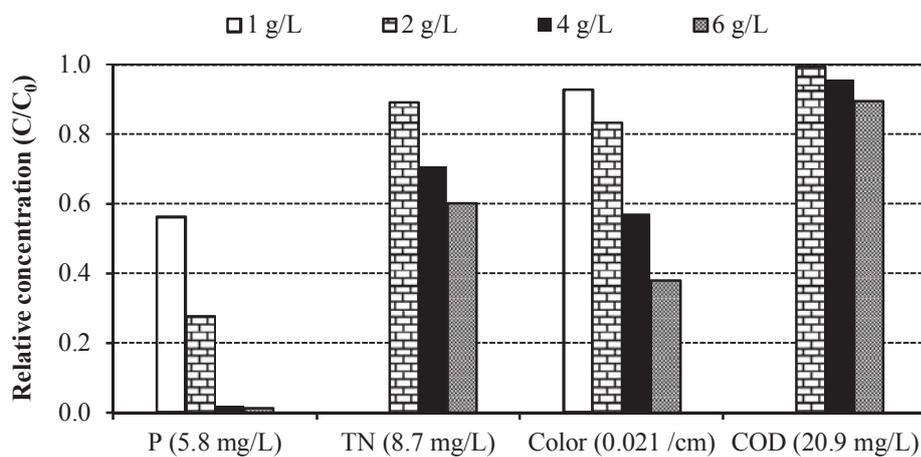
**Fig. 1** – Adsorption of phosphate on Mg-Fe-Cl LDH as a function of (a) LDH dosage; (b) contact time; (c) initial phosphate concentration; (d) initial solution pH.



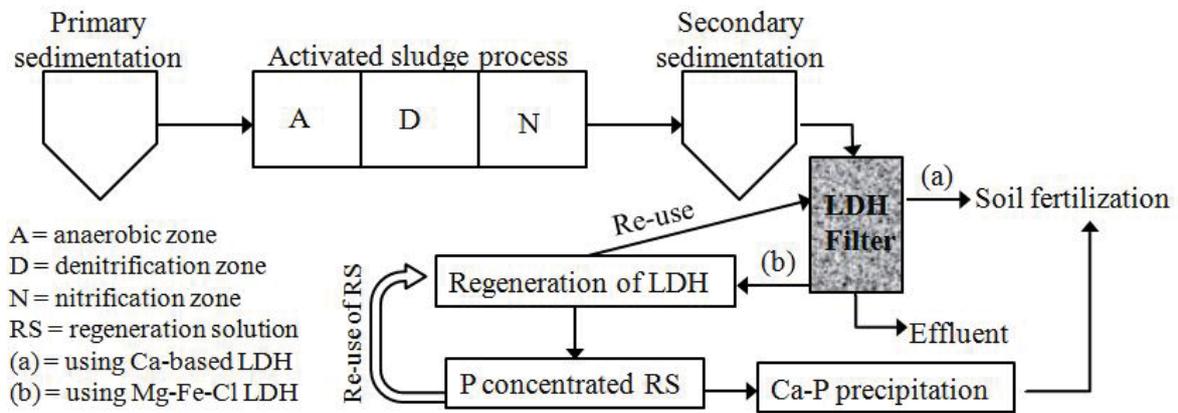
**Fig. 2** – Effect of EBCT on phosphate sorption by Mg-Fe-Cl LDH in fixed bed column test: (a) breakthrough curves; (b) sorption capacity.



**Fig. 3** – Effect of surface loading rate on the treated effluent capacity at different P discharge concentration by Mg-Fe-Cl LDH filled column.



**Fig. 4** – Relative residual concentration of various effluent quality parameters after treated by Mg-Fe-Cl-LDH (initial concentrations in parenthesis).



**Fig. 5** – Possible strategy of using LDH based tertiary treatment step with the conventional WWTP process to achieve future stringent P discharge limit.

**Table 1** – Composition of the Mg-Fe-Cl LDH before and after phosphate uptake.

Element	Before sorption (wt. %)		After sorption (wt. %)	
	LDH-60	LDH-450	LDH-60	LDH-450
O	43.36	40.73	47.17	43.54
Mg	21.41	24.81	20.57	22.33
Fe	24.03	29.79	26.76	31.10
Cl	8.59	3.41	0.15	0
Na	2.61	1.25	1.65	0.46
P	0	0	3.70	2.56
Total (%)	100	100	100	100

**Table 2** – Composition of Mg-Fe-Cl-LDH.

Ion	Dose in preparation (g)	Residual in the supernatant (g)	Content in LDH	
			(g)	(mol)
Mg <sup>2+</sup>	4.9	0.161	4.7	0.195
Fe <sup>3+</sup>	5.6	0.000	5.6	0.100
Cl <sup>-</sup>	24.9	16.072	8.8	0.247
Na <sup>+</sup>	13.8	10.350	3.5	0.150
OH <sup>-</sup>	10.2	–	10.1 <sup>a</sup>	0.594

<sup>a</sup> based on mass and electronic balance

**Table 3** – Kinetic parameters and correlation coefficients ( $R^2$ ) for first-order and pseudo second-order kinetic models.

LDH	$q_e, \text{exp}$ (mg/g)	Pseudo first-order			Pseudo second-order		
		$q_e, \text{cal}$	$k_1$	$R^2$	$q_e, \text{cal}$	$k_2$	$R^2$
		(mg/g)	(1/h)		(mg/g)	(g/mg h)	
Mg-Fe-Cl-60	4.82	1.84	1.59	0.946	5.11	2.01	0.999
Mg-Fe-Cl-450	5.00	0.80	1.31	0.895	5.10	3.75	1

**Table 4** – Isotherm model constants for phosphate adsorption on Mg-Fe-Cl-450 LDH.

LDH	Langmuir isotherm			Freundlich isotherm		
	$q_0$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$	$n$	$R^2$
Mg-Fe-Cl-450	9.8	14.38	0.978	6.9	4.38	0.956