Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22535

127 (2018) 64–70
September

Use of Ca- and Mg-type layered double hydroxide adsorbent to reduce phosphate concentration in secondary effluent of domestic wastewater treatment plant

S.M. Ashekuzzaman, Jia-Qian Jiang*

School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow G4 0BA,
Scotland, UK, Tel. +44 141 331 8850; emails: jiaqian.jiang@gcu.ac.uk (J.-Q. Jiang),

Received 21 December 2017; Accepted 22 May 2018

ABSTRACT

World widely, the excess loads of phosphorus (P) is one of the most common chemical contamination in freshwater bodies (e.g. lakes and rivers), which is one of the major causes of eutrophication. Effluents from wastewater treatment plant (WWTP) 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. In this study, Ca and Mg incorporated layered double hydroxide (LDH) adsorbents were synthesized and assessed for phosphate removal from both P spiked synthetic solution and real effluent sample of a WWTP to provide a comparative overview of using such LDHs as a P removal treatment option in WWTPs. The phosphate removal with Ca-type LDHs were 85%–99%, whereas the removal with Mg-type LDHs were <50% under the same operating conditions, suggesting a significant influence of the type of precursor metals in synthesizing LDH compounds for removing phosphate. However, the Mg-type LDH up to 2 g/L can provide a similar P removal as Ca-type LDHs at the dose of 0.3 g/L to reduce P concentration to 0.1 mg/L from an initial concentration of 10 mg/L. The effluent from WWTP's secondary treatment process with P concentration of 1.4–5.6 mg/L can be treated by both types of LDH to meet future stringent discharge limit at the concentration of 0.1 mg/L. The Mg-type LDH showed mineral stability and regeneration efficiency with ligand exchange and anion exchange as the main mechanism for P removal, while the Ca-type LDH removed P as calcium–phosphate precipitation due to dissolution with broken layered structure in aqueous phase. Overall, both of Ca- and Mg-type LDHs can be potentially applied for tertiary treatment step with the WWTP's conventional treatment process to further polishing P discharge level. But future studies are required to investigate the effect of practical wastewater conditions (medium-term) and estimate costs of application (long-term) of using LDHs for phosphorous removal in real wastewater treatment.

Keywords: Adsorption; Anion exchanger; Layered double hydroxide; Phosphate removal; Wastewater treatment; Secondary effluent

1. Introduction

In recent decades, one of the most common chemical contaminants in freshwater bodies (e.g. lakes and rivers) worldwide is the excess loads of phosphorus (P) [1], which enters water bodies through point sources (e.g. municipal wastewater treatment plants (WWTPs)) and diffuse sources (e.g. agricultural run-off) [2]. The WWTPs 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 or more [3,4]. Excess P in lakes, lagoons and rivers is one of the major causes of eutrophication (known as the process to extensive growth of water plants, algae and plankton) [5]. A minimal amount of phosphorus in water, even at bioavailable P concentration, for example, <0.1 mg/L,

---

* Corresponding author.

Presented at the 15th International Conference on Environmental Science and Technology (CEST-2017), 31 August–2 September 2017, Rhodes, Greece.

with the availability of carbon and nitrogen at C:N:P molar ratio of 105:15:1 can cause substantial algae growth [6], and thereby, subsequent deterioration of water quality and ecological unbalance like depletion of oxygen (causing fish death), production of toxin from some harmful algal blooms, loss of aesthetic value or even loss of water resources can occur [7,8].

The cost of these kinds of damage due to eutrophication to the United Kingdom water industry is estimated at >£15 million annually [9]. The global surface water bodies such as rivers and streams, lakes and reservoirs, and estuaries are facing the risk of eutrophication. The EU considers that lakes with total P concentration <0.01 mg/L is not at risk of eutrophication, and rivers with total P concentration less than 0.01–0.07 mg/L is considered excellent waters [10]. However, in the United Kingdom, 80% of 98 surveyed rivers were found to exceed the accepted standard of healthy rivers' background P concentration, for example, 0.1 mg/L [11]. It has been predicted that eutrophication of surface water and coastal zones will be growing almost everywhere until 2030, with the number of lakes facing harmful algal blooms rising worldwide by 20% or more until 2050 [1].

Due to the growing concern over eutrophication, the discharge level of P from WWTPs in many countries is going to be strictly limited to 0.1 mg/L or even less [4]. However, conventional treatment methods, including biological P removal and precipitation–sorption processes are not capable to reduce P concentrations below 0.1 mg/L in the final effluent due to thermodynamic and kinetic limitations [2]. Moreover, chemical precipitation involves with excessive sludge production, high operating costs and problems of disposing P-rich sludge without further chemical treatment [12,13]. Hence, alternative technologies are sought to enhance the P removal efficiency from WWTPs.

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 remove P from wastewater but also to recover it as secondary P resources (e.g. P-loaded minerals) considering the limited reserve of viable P minerals. Recently, a number of isostructural layered double hydroxide (LDH) based inorganic adsorbents have attracted research interest to remove oxyanion contaminants such as arsenite, arsenate, chromate, selenate, phosphate and borate from aqueous solution [14–19], and these are identified and proposed as a good ion-exchangers and adsorbents, mainly because of their special properties such as high anion exchange capacity, large surface area, good thermal stability and recyclability [20,21]. In principle, LDH compounds consist of positively charged brucite-like ($Mg(OH)_2$) sheets and 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. Based on the general formula of LDH structure, various isostructural LDH compounds can be prepared with great diversity in metal precursors (i.e., cation pairs), intercalated anions and synthesis methods. There is still no specific direction on the selection of particular LDHs considering its application to remove emerging pollutants like phosphorus oxyanions. In previous studies, Mg–Al, Mg–Fe, Ca–Al and Ca–Fe LDHs with CO_3^{2-}or Cl^- as the interlayer anion were mostly assessed for phosphate removal from aqueous solution [15,20]. But the comparative assessment to differentiate the P removal capacity, removal process, aqueous stability, re-usability and applicability of the use of Ca and Mg associated LDHs is limited, which were the objectives of this research. In this study, two types of LDH-based adsorbents (Ca and Mg incorporated) were synthesized and examined for P sorption–desorption process with the consideration that LDH media have the potential to improve P removal in complying with more stringent effluent discharge regulations. Specifically, real wastewater effluent samples were used to assess the performance of the resulting LDHs, developed in this study, for the removal of phosphate and to generate optimal operating conditions.

2. Materials and methods

2.1. Synthesis and chemistry of LDH

Both Ca- and Mg-type LDH compounds were prepared by the coprecipitation method adapting a procedure from Ref. [22] incorporating the most common trivalent (Al^{3+}, Fe^{3+}) metal precursors at two drying temperatures (60°C and 450°C). Herein, the molar ratio of divalent (e.g. Ca^{2+}) to trivalent (e.g. Al^{3+}) was 2:1 and the interlayer anions were selected as NO_3^- and Cl^-. The final LDH products were Ca-based Ca-Al-NO_3, Ca-Fe-NO_3, Ca-Fe-Cl and Mg-based Mg-Al-NO_3, Mg-Fe-NO_3, Mg-Fe-Cl.

The structural patterns of the LDH samples were characterized by X-ray diffraction (XRD) analyses using a Siemens D5000 Diffractometer. The morphology of the LDH samples was examined by scanning electron microscopy (Carl Zeiss EVO50 XVP) equipped with energy dispersive X-ray (EDX) facility (Oxford Instruments X-Max, Resolution 129 eV).

The prepared materials showed the characteristic XRD patterns (e.g. sharp, symmetric, strong lines at low

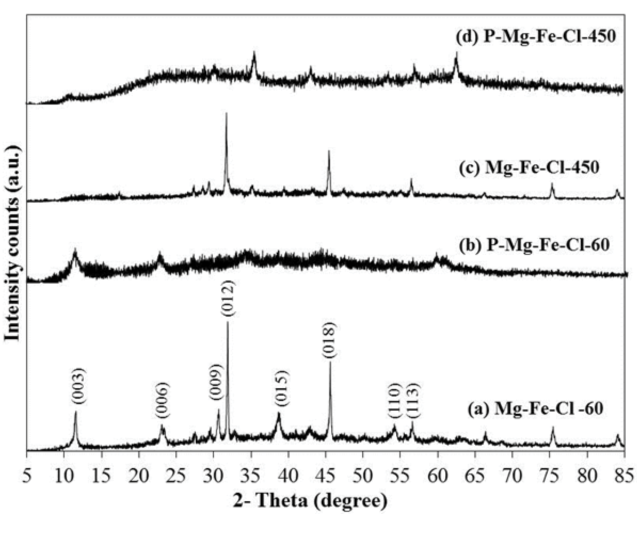

Fig. 1. Powder XRD patterns of Mg type (Mg-Fe-Cl) LDH before (as-prepared) and after P removal.

2θ values and weaker, less symmetric lines at high 2θ values) of a typical LDH structure with easily recognizable Bragg reflections by typical planes of (003), (006) and (110) (Fig. 1). The analysis of EDX spectrum confirmed the presence of major elements in the final product as used during LDH preparation and also, supported the P uptake and removal process (Table 1).

2.2. P removal study using LDH

Batch experiments were conducted to assess P removal by the prepared LDH compounds from both synthetic solution and effluent samples from a WWTP. The factors tested were LDH dose, contact time, pH effect and P concentration levels. Also, desorption of P and re-usability of LDH compound were assessed under batch study mode. A stock solution of $NaH_2PO_4 \cdot H_2O$ dissolved in deionized water at 50 mg-P/L was made up and the working synthetic solutions with desired P concentration were made from the stock. The pH of working solutions was adjusted manually to the required values with diluted NaOH or HCl solutions.

Domestic sewage effluent after secondary treatment process prior to discharge point to the river was collected from Shieldhall Waste Water Treatment Works (WWTW) at Glasgow, Scotland (UK) for treating with selected LDH. Samples were analysed for desired parameters in the same day of collection and kept in the refrigerator at 4°C for further experiments. These parameters were determined according to the standard methods for the examination of waters and wastewater [12]. The major water quality parameters in three collected samples were in the range as follows: pH = 6.8–7.3, turbidity (NTU) = 1–3, total suspended solids (mg/L) = 1.8–6.1, dissolved reactive P (mg/L) = 1.4–5.6, total N (TN, mg/L) = 3.7–8.8, COD (mg O_2/L) = 21–27.

The batch sorption study protocol was as follows: LDH compounds were mixed with 25 mL of phosphate solution ($[P_o]$ = 10 mg P/L, pH_o = 7) in 50 mL screw top polypropylene conical tubes using rotary shaker, and subsequently, centrifuged, filtered and finally, residual P concentrations were measured by ascorbic acid method [23] using UV-Vis spectrophotometer at 880 nm. The results are presented as the average of duplicate trials, and the reproducibility of the results were varied within the standard deviation <±5%. The adsorption capacity (Q_e, mg/g) or quantity of P adsorbed by the sorptive media, and removal rate (R) of P were calculated from the following relations:

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

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).

To identify 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. The concentration of various ions (e.g. Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cl^- and NO_3^-) in the aqueous phase was determined by RFID enabled HACH DR3900 spectrophotometer using respective calibrants supplied by HACH Lange, UK.

In sorption–desorption cycle, phosphate saturated LDH was separated after sorption phase and subsequently, used for desorption phase using selected desorbing solution (4% NaOH) followed by centrifugation and washing. 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 selected LDHs were regenerated up to some appropriate cycles considering the consistency of sorption performance.

Table 1
Composition of the Ca- and Mg-type LDHs before and after phosphate uptake

Element	Before sorption (%)		After sorption (%)	
	Ca-Fe-Cl[a]	Mg-Fe-Cl[b]	Ca-Fe-Cl	Mg-Fe-Cl
O	58.90	61.91	53.50	65.97
Ca or Mg	12.99	20.13	27.90	18.94
Fe	6.51	9.83	10.65	10.72
Cl	9.64	5.53	0	0.09
Na	11.96	2.60	0.85	1.61
P	0	0	7.10	2.67
Total (%)	100	100	100	100

[a]Synthesized at 450°C; [b]Synthesized at 60°C.

3. Results and discussion

3.1. Factors associated with the P removal by LDH

P removal was significantly higher by Ca-type LDHs (i.e., Ca-Al-NO_3, Ca-Fe-NO_3 and Ca-Fe-Cl) than those of Mg type (i.e., Mg-Al-NO_3, Mg-Fe-NO_3 and Mg-Fe-Cl) under the same operating conditions (e.g. at same dose) (Table 2). Where the P removal trend flattened out an optimal dose for each LDH was selected. Results showed that Ca-type LDHs removed 98%–99% of P at dose of 0.3 g/L from synthetic solution of 10 mg-P/L, whereas Mg type removed only up to 22%. In comparison with the optimal adsorbent dose of Ca-LDHs, Mg type for example, Mg-Fe-Cl LDH was observed to require much higher optimal dose as 2 g/L to achieve about 99% removal of phosphate. The removal performance due to the incorporation of either Al or Fe as trivalent cation with either LDH type was insignificant as was the case for either intercalated anion of NO_3^- or Cl^-. Also, LDHs synthesized at 450°C were not found to improve the sorption performance significantly than those synthesized at 60°C. These results have clearly demonstrated the influence and selection of Ca and Mg as precursor metals in synthesizing LDH compounds for removing phosphate.

The equilibrium time required for the adsorption of P was almost 2 h and the removal rate was about 98%–99% by this time. So, all the further adsorption experiments were conducted at 2 h contact time. First-order and pseudo-second-order kinetic models were used to analyse the

Table 2
Removal of phosphate (%) from 10 mg-P/L synthetic solution by various Ca- and Mg-type LDHs (adsorbent dose = 0.3 g/L, pH = 7)

LDHs	LDHs synthesized at	
	60°C	450°C
Ca-Al-NO_3	99.1 ± 0.3	99.5 ± 0.0
Ca-Fe-NO_3	99.2 ± 0.3	99.0 ± 0.2
Ca-Fe-Cl	97.8 ± 0.4	–[a]
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	–

SD = standard deviation (n = 3), [a]Data not available.

sorption kinetics and it was found that the sorption kinetics of phosphate on both LDH types were well governed by the pseudo-second-order kinetic model, suggesting that chemisorption process (bond formation at LDH's surface) occurred for phosphate uptake.

The study on pH effect of adsorbate solution suggested that P adsorption for Ca-type LDHs was almost steady (~98%) in the range of pH between 3.5 and 10.5, whereas for Mg type, it was at pH between 3 and 7.5 (Fig. 2). With further increase in pH up to 12.0, there was a steady decrease. This is in conformity with two facts: (1) higher pH causes increasing competition for adsorption sites between OH^- groups and phosphate species (e.g. HPO_4^{2-} at pH > 7.0) and (2) a higher pH can cause the adsorbent surface to carry more negative charges (e.g. when point of zero charge (pH_{pzc}) of sorbents is less than solution pH) and thus would enhance repulsive interaction between the adsorbent surface and the anions in solution [24]. Moreover, the equilibrium (eql.) pH was observed to be raised about 10.5 and 9.9 for an initial pH range of 3.5–10.5 and 3–7.5, respectively, for Ca-type and Mg-type LDHs, with no significant changes observed in the removal rate for such a wide initial pH range (Fig. 2). So, these results indicate a strong buffering capacity of both LDHs, and suggest that LDHs of Mg type could be useful for phosphate removal in domestic WWTW (pH usually ranged at 6.8–7.2) without prior pH adjustment, while Ca type have greater applicability under different pH system.

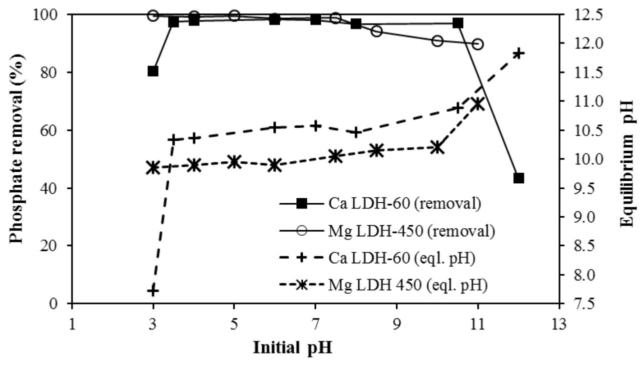

Fig. 2. Effect of pH on phosphate removal by Ca and Mg incorporated LDH (dosage was 0.3 g/L for Ca-type LDH and 2 g/L for Mg-type LDH, $[P_o]$ = 10 mg/L, T = 2 h).

The effect of initial phosphate concentration on its adsorption by selected LDH type was studied at optimum adsorbent dosage (0.3 g/L for Ca type and 2 g/L for Mg type). 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. The adsorption data were fitted to the Langmuir and Freundlich isotherm model relationships and values of isotherm constants are shown in Table 3. The adsorption isotherms can be better predicted by the Langmuir model for both LDH types as observed from the greater correlation coefficients (R^2) to those in Freundlich fitting.

The adsorption capacity of phosphate on Ca LDH is much higher than that on Mg LDH, for example, the maximum adsorption capacity on Ca-Al-NO_3 is 66.7 mg-P/g, while on Mg-Fe-Cl is only 9.8 mg-P/g as per Langmuir model. The maximum P adsorption capacity by the LDHs also varied (e.g. between 4.3 and 140.7 mg-P/g LDH) 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 studied and the experimental approaches used. In general, the removal performance of phosphate obtained in this study is higher than that of some commonly available adsorbents and also comparable with some of the relevant LDHs in the literature (Table 4). It can be observed that removal performance in terms of removal rate and sorption capacity is highly variable in relation to the use of adsorbent dose and adsorbate initial concentration.

Table 3
Isotherm model constants for phosphate adsorption on selective LDHs

Isotherm model	Ca- and Mg-type LDHs	
	Ca-Al-NO_3	Mg-Fe-Cl
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	9.8
b (L/mg)	7.64	14.38
R^2	0.9972	0.9786
Freundlich isotherm $\left(\log q_e=\log K_f+\frac{1}{n}\log C_e\right)$		
K_f	43.7	6.9
n	4.09	4.38
R^2	0.9124	0.9563

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.

Table 4
Comparative P removal performance of some common adsorbents and relevant LDH compounds

Adsorbent media	Dose (g/L)	[C_o] (mg/L)	pH_o	pH_e	Time (h)	Removal[a] (%)	Q_{max} (mg/g)	Reference
Iron oxide coated crushed brick	20	9.8	5	>8	2	76.0	1.75	[25]
Activated alumina	5	10	3–4	–	24	80.0	3.33	[26]
Fly ash	100	1000	12	9.5	24	99.0	23.2	[27]
Blast furnace slag	60	180	8.5	–	1	99	6.37[b]	[28]
$Mg_2Fe(Cl)$-50 LDH	0.2	45	8	9.5	24	4.7	10.5[c]	[15]
$Ca_2Fe(Cl)$-50 LDH	0.2	45	8	10.5	24	25.1	56.4[c]	[15]
$Ca_2Al(NO_3)$-60 LDH	0.3	30	7	9.7	2	66.7	66.7	This study
$Ca_2Fe(NO_3)$-60 LDH	0.3	30	7	9.5	2	47.4	47.4	This study
$Mg_2Fe(Cl)$-60 LDH	2	10	7	9.9	3	99.0	9.8	This study

pH_o = initial solution pH; pH_e = equilibrium solution pH; [a]Equilibrium removal efficiency; Q_{max} = maximum adsorption capacity from Langmuir isotherm; [b]Based on Freundlich isotherm; [c]Experimental maximum adsorption capacity.

Both Ca- and Mg-type LDHs were assessed for re-usability through sorption–desorption phase. It was found that P sorption efficiency of Ca-LDH decreased significantly from 99% to about 30% when re-used after first regeneration. As a result, this was not considered for further cycles. On the other hand, repeated use of Mg-LDH showed comparatively consistent P removal up to six cycles of sorption–desorption study. In this case, the sorption capacity was decreased by 14% after six cycles of sorption run in comparison with that of pristine LDH (from about 5 to 4.3 mg-P/g of LDH).

The physicochemical features of Ca-LDHs revealed that these are instable in aqueous phase and cannot be re-used followed by adsorption, desorption and regeneration cycles due to loss of layered structure after first sorption operation. For example, a mass loss of 32%–53% was observed with Ca incorporated LDHs due to the occurrence of major ion release. In comparison, Mg incorporated LDHs showed the lowest ion release tendency. This might be related to the selection of divalent cations, that is, 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 as divalent precursor due to the higher solubility product of $Ca(OH)_2$ (K_{sp} = 5.02 × 10^{-6}) than $Mg(OH)_2$ (K_{sp} = 5.61 × 10^{-12}) [29]. The analysis of various ions in the supernatant after first adsorption–desorption cycle also confirmed that >50% of pristine Ca-LDH mass was lost during the process compared with only about 7% mass loss from Mg-LDH, indicating the better aqueous stability of the later type. Mg-LDH was observed to be stable with only 1.2% of the Mg^{2+} or Fe^{3+} ions release during first sorption run, followed by almost negligible (~0.5%) ion release in the second sorption run. The P removal process with Ca-LDHs was mainly due to calcium–phosphate precipitation and this could be the reason of their much higher sorption capacity than Mg-LDHs. In contrary, the removal mechanism of phosphate by Mg-LDH was predominantly due to ligand exchange by OH^- ions on the LDH surface and anion exchange with Cl^- in the interlayer region.

3.2. LDH application to treat secondary effluent

Real effluent (both undisturbed and spiked up to ~10 mg-P/L) from WWTW was used to study the P removal by Ca- and Mg-type LDHs (e.g. Ca-Al-NO_3 and Mg-Fe-Cl) and the results are shown in Fig. 3. It is clearly evident that effluent with low-to-high P concentration can be treated successfully by both types 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-LDH at 1.5 g/L dose from effluent with P concentration of 3.4–10.4 mg/L. In comparison with Ca type, Mg-LDH removed above 98% at adsorbent dose of 4 g/L from effluent with 5.6 mg-P/L. This indicates that at least twofold higher dose was required for Mg-LDH to attain the similar phosphate removal efficiency as that from the test solution. The presence of other parameters such as TN and colour were also somewhat removed (about 30%–60%) with increasing LDH dose above 2 g/L. This explains why comparatively higher dose of LDH could be required to achieve comparable P removal from real effluent with that from test solution containing only phosphate.

3.3. Applicability

It was found that P level can be lowered to 0.1 mg/L by using both Ca-type (Ca-Al(NO_3)) and Mg-type (Mg-Fe(Cl)) LDHs from test solution with an initial concentration of 10 mg-P/L at the adsorbent dosage of 0.3 and 2 g/L, respectively. Also, both of these LDHs can remove P unaffected for the pH range between 3.5 and 7.5, which is suitable for treating secondary effluent of WWTP. The effluent from WWTP's secondary treatment process with P concentration of 1.4–5.6 mg/L can be treated by the prepared LDHs to meet future stringent discharge limit depending on the selection of suitable adsorbent dose. Based on the P removal performance and mechanism of Ca- and Mg-LDHs, these LDHs can be potentially applied for tertiary treatment step with the WWTP's conventional treatment process to further polishing P discharge level. For example, the effluent of WWTP after secondary sedimentation process can be treated with LDH-based materials in a filtration unit, for example, by using Ca-type LDH to achieve effluent P concentration of 0.1 mg/L and consequently, recovering P in the filtration unit as Ca–P solids after one cycle, which can be re-used as P-loaded minerals. In case of Mg-type LDH, it can be regenerated and

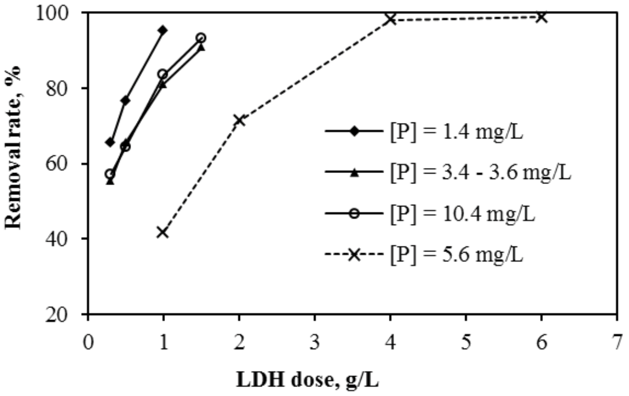

Fig. 3. Phosphate removal from effluent with different starting P concentration as a function of dose (pH$_o$ = 7.1 ± 0.4, T = 2 h). Solid and doted lines, respectively, indicate the removal by Ca-Al-NO$_3$ and Mg-Fe-Cl LDHs.

re-used for P sorption for several cycles (six regenerations) using suitable desorbing solution (4% NaOH) as observed in this study. It means P can be concentrated in the desorbing solution and subsequently, can be precipitated from P-rich alkaline solution using CaCl$_2$ and recovered as Ca–P solids [30,31]. The advantage of using LDH-based filtration media will be not only to meet stringent 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.

4. Conclusions

LDH-based adsorbent media are of two types: Ca and Mg incorporated LDHs were prepared and assessed for P sorption–desorption process. Results demonstrated that both types LDHs can reduce P level down to 0.1 mg/L from synthetic solution of 10 mg-P/L at the adsorbent dose of 0.3 and 2 g/L, respectively. Also, both of these LDHs can remove P unaffected for the pH range between 3.5 and 7.5, which is suitable for treating secondary effluent of WWTP. The effluent from WWTP's secondary treatment process with P concentration of 1.4–5.6 mg/L can be treated by the prepared LDHs to meet future stringent discharge limit depending on the selection of suitable adsorbent dose. For example, Mg-Fe-Cl removed above 98% at dose of 4 g/L from effluent with 5.6 mg-P/L and Ca-Al-NO$_3$-60 removed about 96% at dose of 1 g/L from effluent containing 1.4 mg-P/L. These LDHs can be potentially applied for tertiary treatment step with the WWTP's conventional treatment process to further polishing P discharge level. These findings can be further capitalized to find out cheap raw materials for cost-effective synthesis, and to conduct pilot-scale assessment to estimate potential costs for practical application in WWTP as P discharge polishing process.

Acknowledgement

Authors are grateful to Glasgow Caledonian University for providing a PhD studentship to S.M. Ashekuzzaman.

References

[1] UNWWAP, The United Nations World Water Development Report 2015: Water for a Sustainable World, UNESCO, Paris, 2015.

[2] B.K. Mayer, D. Gerrity, B.E. Rittmann, D. Reisinger, S. Brandt-Williams, Innovative strategies to achieve low total phosphorus concentrations in high water flows, Crit. Rev. Env. Sci. Technol., 43 (2013) 409–441.

[3] POST note 477, Phosphate Resources, The Parliamentary Office of Science and Technology, 7 Millbank, London, UK, 2014.

[4] S.K. Zheng, J.J. Chen, X.M. Jiang, X.F. Li, A comprehensive assessment on commercially available standard anion resins for tertiary treatment of municipal wastewater, Chem. Eng. J., 169 (2011) 194–199.

[5] L. Rafati, R. Nabizadeh, A.H. Mahvi, M.H. Dehghani, Removal of phosphate from aqueous solutions by iron nano-particle resin Lewatit (FO36), Korean J. Chem. Eng., 29 (2012) 473–477.

[6] J.-Q. Jiang, O. Mwabonje, Phosphorus recovery by liquid-liquid extraction, Sep. Sci. Technol., 44 (2009) 3258–3266.

[7] Z. Wen, Y. Zhang, C. Dai, Removal of phosphate from aqueous solution using nanoscale zerovalent iron (nZVI), Colloids Surf., A, 457 (2014) 433–440.

[8] H. Gharibi, A.H. Mahvi, M. Chehrazi, R. Sheikhi, S.S. Hosseini, Phosphorous removal from wastewater effluent using electro-coagulation by aluminum and iron plates, Anal. Bioanal. Electrochem., 2 (2010) 165–177.

[9] X. Song, Y. Pan, Q. Wu, Z. Cheng, W. Ma, Phosphate removal from aqueous solutions by adsorption using ferric sludge, Desalination, 280 (2011) 384–390.

[10] European Commission, Guidance Document on Eutrophication Assessment, Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Document No 23, Technical Report, 2009.

[11] C. Pratt, S.A. Parsons, A. Soares, B.D. Martin, Biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater, Curr. Opin. Biotechnol., 23 (2012) 890–896.

[12] S.A. Parsons, J.A. Smith, Phosphorus removal and recovery from municipal wastewaters, Elements, 4 (2008) 109–112.

[13] A.H. Mahvi, S.J.A. Ebrahimia, A. Mesdaghinia, H. Gharibia, M.H. Sowlata, Performance evaluation of a continuous bipolar electrocoagulation/electrooxidation–electroflotation (ECEO–EF) reactor designed for simultaneous removal of ammonia and phosphate from wastewater effluent, J. Hazard. Mater., 192 (2011) 1267–1274.

[14] J.-Q. Jiang, S.M. Ashekuzzaman, Development of novel inorganic adsorbent for water treatment, Curr. Opin. Chem. Eng., 1 (2012) 191–199.

[15] J. Zhou, Z.P. Xu, S. Qiao, Q. Liu, Y. Xu, G. Qian, Enhanced removal of triphosphate by MgCaFe-Cl-LDH: synergism of precipitation with intercalation and surface uptake, J. Hazard. Mater., 189 (2011) 586–594.

[16] X. Cheng, X. Huang, X. Wang, D. Sun, Influence of calcination on the adsorptive removal of phosphate by Zn–Al layered double hydroxides from excess sludge liquor, J. Hazard. Mater., 177 (2010) 516–523.

[17] F.L. Theiss, S.J. Couperthwaite, G.A. Ayoko, R.L. Frost, A review of the removal of anions and oxyanions of the halogen elements from aqueous solution by layered double hydroxides, J. Colloid Interface Sci., 417 (2014) 356–368.

[18] Y. Guo, Z. Zhu, Y. Qiu, J. Zhao, Adsorption of arsenate on Cu/Mg/Fe/La layered double hydroxide from aqueous solutions, J. Hazard. Mater., 239–240 (2012) 279–288.

[19] J. Zhou, Y. Su, J. Zhang, X. Xu, J. Zhao, G. Qian, Y. Xu, Distribution of OH bond to metal-oxide in Mg$_{3-x}$Ca$_x$Fe-layered double hydroxide (x = 0–1.5): its role in adsorption of selenate and chromate, Chem. Eng. J., 262 (2015) 383–389.

[20] X. Sun, T. Imai, M. Sekine, T. Higuchi, K. Yamamoto, A. Kanno, S. Nakazono, Adsorption of phosphate using calcined Mg$_3$-Fe layered double hydroxides in a fixed-bed column study, J. Ind. Eng. Chem., 20 (2014) 3623–3630.

[21] K.H. Goh, T.T. Lim, Z.L. Dong, Removal of arsenate from aqueous solution by nanocrystalline Mg/Al layered double

hydroxide: sorption characteristics, prospects and challenges, Water Sci. Technol., 61 (2010) 1411–1417.

[22] J.-Q. Jiang, Y. Xu, K. Quill, J. Simon, K. Shettle, Laboratory study of boron removal by Mg/Al double-layered hydroxides, Ind. Eng. Chem. Res., 46 (2007) 4577–4583.

[23] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington DC, 2005.

[24] P. Cai, H. Zheng, C. Wang, H. Ma, J. Hu, Y. Pu, P. Liang, Competitive adsorption characteristics of fluoride and phosphate on calcined Mg-Al-CO_3 layered double hydroxides, J. Hazard. Mater., 213–214 (2012) 100–108.

[25] N. Boujelben, J. Bouzid, Z. Elouear, M. Feki, F. Jamoussi, A. Montiel, Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents, J. Hazard. Mater., 151 (2008) 103–110.

[26] J. Wang, Y. Zhang, C. Feng, J. Li, G. Li, Adsorption capacity for phosphorus comparison among activated alumina, silica sand and anthracite coal, J. Water Res. Prot., 4 (2009) 260–264.

[27] P. Pengthamkeerati, T. Satapanajaru, P. Chularuengoaksorn, Chemical modification of coal fly ash for the removal of phosphate from aqueous solution, Fuel, 87 (2008) 2469–2476.

[28] E. Oguz, Removal of phosphate from aqueous solution with blast furnace slag, J. Hazard. Mater., B114 (2004) 131–137.

[29] J.Z. Zhou, Z.P. Xu, S. Qiao, J. Liu, Q. Liu, Y. Xu, J. Zhang, G. Qian, Triphosphate removal processes over ternary CaMgAl-layered double hydroxides, Appl. Clay Sci., 54 (2011) 196–201.

[30] E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B.V. der Bruggen, W. Verstraete, K. Rabaey, B. Meesschaert, Global phosphorus scarcity and full-scale P-recovery techniques: a review, Crit. Rev. Env. Sci. Technol., 45 (2015) 336–384.

[31] A. Tolkou, A. Zouboulis, C. Raptopoulou, Phosphorus Recovery in Wastewater Treatment: Moving from Lab to Pilot Scale, Proceedings of the World Congress on New Technologies (NewTech), Barcelona, Spain, July 15–17, 2015, Paper no. 157.