Phosphate adsorption from sewage sludge filtrate using zinc–aluminum layered double hydroxides

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ABSTRACT

A series of layered double hydroxides (LDHs) with different metal cations were synthesized to remove phosphate in waste sludge filtrate from a municipal wastewater treatment plant for phosphorus recovery and to help control eutrophication. The highest phosphate adsorption capacity was obtained by using Zn–Al-2-300, that is LDHs with Zn/Al molar ratio of 2 and calcined at 300 °C for 4 h. Circumneutral and mildly alkaline waters appeared suitable for the possible application of Zn–Al LDHs due to the amphoteric nature of aluminum hydroxide. Phosphate adsorption from the sludge filtrate by the LDHs followed pseudo-second-order kinetics, and the adsorption capacity at equilibrium was determined to be ~50 mg P/g. Adsorption isotherms showed that phosphate uptake in this study was an endothermic process and had a good fit with a Langmuir-type model. The absorbed phosphate can be effectively desorbed (more than 80%) from LDHs particles by a 5 wt% NaOH solution. The regeneration rate of used LDHs was ~60% after six cycles of adsorption–desorption–regeneration.

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1. Introduction

Waste streams from industrial, agricultural and household activities contain considerable amount of soluble phosphate, and its discharge to receiving waters could result in eutrophication of rivers, lakes and bays [1]. Currently biological nutrient removal processes are employed as the main methods for phosphate separation from wastewaters. However, the application of these methods does not perfectly resolve the problem because of environmental risks and safety concerns in disposal of these sludges containing condensed phosphate, heavy metals and microorganisms.

On the other hand, phosphorus is essential for all forms of life. Phosphorus plays an important role in DNA/RNA molecules and is also related to cellular energy transport via ATP. Unfortunately, phosphorus as a resource is nonrenewable and nonreplaceable. Under present technological and economic conditions the known supply of phosphorus is estimated to meet the demand for only around one century; this includes large amounts found in low-grade rock [2]. Most of phosphorus in nature will end up in deep marine sediments, reentering the cycle probably after millions of years.

Therefore, it is urgent to protect, recover and reuse this limited resource for the sustainable development of the globe.

Chemical precipitation has been well documented as a popular technology for phosphate recovery from wastewater in pilot- and a few full-scale evaluations [3,4]. It is fairly controllable and will produce high-quality of phosphate precipitates, typically struvite. Precipitation incurs a cost for treatment chemicals and also a large volume of chemical sludge, which becomes a disposable problem. More recently some researchers studied the feasibility of phosphate adsorption from phosphate-rich streams. The various adsorbents used include industrial materials and byproducts (i.e., iron oxide tailings [5], fly ash [6], blast furnace slag [7] and red mud [8]), natural or synthetic minerals (i.e., goethite [9,10], dolomite [11] and alunite [12]), metal oxide/hydroxide (i.e., aluminum oxide, iron oxide, zirconium oxide [13] and zirconium hydroxide [14]) and other materials (i.e., ion exchange resin [15]).

Layered double hydroxides (LDHs), also called hydrotalcite-like compound or anionic clay, have received wide attention as an effective adsorbent. The formula can be normally expressed as $[M_{1-x}M_x^{3+}(\text{OH})_2][A^{n-}]_{x/n} \cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent metal cations in the octahedral positions of the positively charged brucite-like layers, A^{n-} is the incorporated anions in the interlayer space along with water molecules for charge neutrality and structure stability, and x normally ranges from 0.17 to 0.33 [16]. Due to the high charge density of the sheets from M^{2+} substitution by M^{3+} and the exchangeability of the interlayer anions

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as well, LDHs have been employed in several studies for removing phosphate in different environment, such as phosphate solutions [13,17–19], drain effluent [20] and seawater [21].

In secondary/enhanced biological processes in municipal sewage works, various forms of phosphorus in water become concentrated in the waste sludge. When exposed to anaerobic conditions, the assimilated phosphorus tends to be released once again, giving rise to a higher concentration of soluble phosphate in the sludge filtrate. The Institute for European Environmental Policy estimated that full application of the Urban Waste Water Treatment Directive 91/271 (EU legislation) would result in a total or around 220–240,000 tonnes phosphates (P) per year being transferred into and removed via sewage sludges [22]. However, to our knowledge, there is no report as yet available on phosphate adsorption from sewage sludge filtrate by LDHs, probably because the high levels of suspended solids in that stream easily clogged the experimental adsorption columns. In the present study, we used magnetic particles-amended LDHs to remove phosphate in sludge filtrate from a sewage treatment plant. The particles were then effectively separated by a magnetic-field for phosphate recovery. Furthermore, factors influencing the adsorption and recovery processes were investigated.

2. Materials and methods

2.1. Preparation of LDHs

A series of LDHs were synthesized by coprecipitation method using various divalent (Mg, Zn, Cu, Ni and Co) and trivalent (Al, Fe) metal cations, and were abbreviated as M(II)–M(III). 200-ml solutions of mixed metal chlorides were prepared in a 500-ml beaker containing 0.5 M of M(II) and variable amount of M(III) (according to the desired M(II)/M(III) ratios). Fe_3O_4 powder was introduced as magnetic core for LDHs particle formation. Under vigorous mechanical stirring, a 20% NaOH solution was then added dropwise through a peristaltic pump to reach final pH of 9.0 ± 0.2 . The synthesis was performed at 80°C in a water thermostat, followed by aging for 18 h at the same temperature. The resulting slurry was filtered and rinsed with deionized water thoroughly until no chloride ion was detected. After drying at 80°C overnight, the precipitate was ground to ~ 100 - μm particles. A portion of the obtained LDHs particles was calcined in an atmosphere of high-purity nitrogen for 4 h to study its effect on the adsorption capacity of the resulting particles. All chemicals used were at least analytical reagent grade except the Fe_3O_4 powder being chemical grade.

2.2. Phosphate adsorption from sewage sludge filtrate

Adsorption assays were carried out in a thermostatic shaker at room temperature. A mass of 0.02 g of LDHs particles were added to 117-mL glass serum vials with 50 mL of sludge filtrate (from Taiping municipal wastewater treatment plant, Harbin, China) and sealed with butyl rubber stoppers. The water quality of the sludge filtrate is shown in Table 1. No pH adjustment (except during the assays of pH effect) or other adjustments were made to the filtrate. After 24 h adsorption, the supernatant was immediately filtered through a 0.45 - μm membrane for complete particle removal. The resulting liquid was used to determine the residual phosphate and then calculate the adsorption capacity of the LDHs. LDHs-free vials were prepared as a control to observe non-adsorptive removal (degradation) of phosphate in the water. All assays were conducted in triplicate. Phosphate adsorption kinetics were investigated similarly, except that 0.1 g of LDHs and 250 mL of the sludge filtrate were used, and the phosphate concentration in liquid was followed for 72 h.

Table 1

Characteristics of sludge filtrate from Taiping municipal wastewater treatment plant, Harbin, China.

Parameter	Sludge filtrate	Parameter	Sludge filtrate
pH	6.80 ± 0.00	Na^+ , mg/L	83.65 ± 0.19
SS, mg/L	3.82 ± 0.00	K^+ , mg/L	44.66 ± 0.05
COD, mg/L	514.62 ± 6.24	Al^{3+} , mg/L	0.06 ± 0.00
PO_4^{3-} , mg P/L	20.00 ± 4.10	Ca^{2+} , mg/L	105.80 ± 0.60
NO_2^- , mg/L	ND ^a	Cu^{2+} , mg/L	ND ^a
NO_3^- , mg/L	ND ^a	Fe, mg/L	0.24 ± 0.00
SO_4^{2-} , mg/L	112.53 ± 0.42	Mg^{2+} , mg/L	27.22 ± 0.09
Cl^- , mg/L	81.44 ± 0.50	Mn^{2+} , mg/L	1.34 ± 0.01
NH_4^+ , mg/L	84.34 ± 4.82	Zn^{2+} , mg/L	0.01 ± 0.00

^a ND: non-detectable.

2.3. Effect of pH on phosphate adsorption

The pH dependence of phosphate adsorption by LDHs was evaluated in batch assays with sludge filtrates from pH 2–12. The pH was adjusted using 1 M HCl/NaOH solution. The phosphate residue in the solution was measured and the concentrations of metal ions were analyzed to estimate the LDH dissolution.

2.4. Study of adsorption isotherm

Adsorption isotherms were obtained by mixing known amounts of LDHs particles with 250 mL of sludge filtrates in 583-ml glass infusion bottles and stirring at fixed temperatures. Residual phosphate was measured after 72 h when adsorption equilibrium was nearly achieved based on the foregoing investigation. Isotherms of phosphate adsorption in KH_2PO_4 solutions (with the same phosphorus concentration as in the sludge filtrate: 20 mg P/L) were also produced for comparison.

2.5. Study of LDHs recovery and phosphate desorption

Phosphate-loaded LDHs were obtained by mixing Zn–Al-2-300 (Zn–Al LDHs with Zn/Al molar ratio of 2, calcined at 300°C) with sludge filtrate at room temperature for 24 h. The particles were separated from the solution by imposing a magnet field, then washed in deionized water several times, and dried at 80°C . An equal amount of the recovered solids were added to three types of desorbent solutions over a range of concentrations (Table 2) to evaluate phosphate desorption. After 24 h of interaction at room temperature, the supernatant was sampled to determine the extent of phosphate release. The resulting LDHs particles were again separated, washed, dried and then regenerated by calcination. The cycle of adsorption, desorption and regeneration was performed seven times using a 5% NaOH solution as a desorbent.

Table 2

Selection of solutions for phosphate desorption from LDHs particles.

Desorption solutions	Desorption rate (%)	Zn^{2+} (mg/L)	Al^{3+} (mg/L)
1% (w/v) NaOH	20.58	23.90	16.75
2% (w/v) NaOH	37.99	54.00	34.18
3% (w/v) NaOH	52.27	65.40	33.70
5% (w/v) NaOH	87.57	85.00	36.12
10% (w/v) NaOH	89.34	333.10	61.17
20% (w/v) NaOH	91.24	426.60	66.12
5% (w/v) NaCl	7.56	3.20	30.54
10% (w/v) NaCl	10.34	8.70	30.49
20% (w/v) NaCl	21.17	9.50	30.19
5% (w/v) NaCO_3	40.34	41.34	20.11
10% (w/v) NaCO_3	84.22	100.35	43.06

The recovery rate (R_{rec}), desorption rate (R_{des}) and regeneration rate (R_{reg}) were estimated using the following equations:

$$R_{\text{rec}(i)} = \frac{L_{(i+1)}}{L_{(i)}} \times 100 \quad (1)$$

$$R_{\text{des}(i)} = \frac{Q_{\text{des}(i)}}{Q_{\text{ads}(i)}} \times 100 \quad (2)$$

$$R_{\text{reg}(i)} = \frac{Q_{\text{ads}(i+1)}}{Q_{\text{ads}(i)}} \times 100 \quad (3)$$

where $L_{(i)}$: the amount of the adsorbent used in the i th adsorption assay (g); $Q_{\text{ads}(i)}$: phosphate uptake in the i th adsorption operation (mg P/g adsorbent); $Q_{\text{des}(i)}$: phosphate desorbed in the i th desorption operation (mg P/g adsorbent).

2.6. Analysis

2.6.1. Characterization of LDHs

Metal ions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer, USA). Crystal phases of LDHs were determined using an X-ray diffractometer (D/Max-RB, Rigaku, Japan) with $\text{CuK}\alpha$ radiation and operating at 45 kV and 45 mA. Samples were prepared as finely pressed LDHs powder in an aluminum holder. XRD patterns were collected over a 2θ from 10° to 90° in a scan rate of $5^\circ/\text{min}$. Thermogravimetry and differential thermal analysis (TG–DSC) were carried out on a STA449C instrument (NETZSCH, Germany). A mass of 4.675 mg of LDHs particles in an open Al_2O_3 crucible were heated from 35 to 1000°C ($10^\circ\text{C}/\text{min}$) in an Ar atmosphere at a flow rate of 30 mL/min.

2.6.2. Phosphate measurement

Water samples were filtered through $0.45\text{-}\mu\text{m}$ membranes to remove suspended solids. The filtrate was then used to determine the concentration of soluble phosphate by the molybdenum blue method [23]. No pH adjustment was conducted except in desorption assays where the pH value of the samples was adjusted to 7.0 ± 0.1 due to their strong alkalinity.

3. Results and discussion

3.1. Parameters affecting phosphate adsorption from sewage sludge filtrate by LDHs

3.1.1. Metal composition

LDHs particles prepared with various metal cations were subjected to phosphate adsorption assays. As shown in Fig. 1, Zn–Al LDHs had the highest adsorption capacity of up to 24.98 mg P/g adsorbent in the sewage sludge filtrate with an initial phosphate concentration of 16.06 mg P/L , followed closely by Mg–Fe and Zn–Fe particles. Low phosphate uptake was observed when Cu, Ni or Co was the divalent cation for LDHs synthesis. The results found here differ from those in similar documents. Das et al. [19] reported that Mg–Al LDHs was the most efficient adsorbent for phosphate removal in a potassium dihydrogen phosphate solution. Chitrakar et al. [21] suggested that a Mg–Mn type and its heat-treated materials were more effective for adsorbing phosphate from seawater. In fact, phosphate uptake by layered double hydroxides in an aquatic environment, especially real waters, is as yet far from well understood; the difference in those results may be related to many specific conditions since in every study the synthesis method of LDHs and the water environment tested and coexisting anions all could be very different.

Fig. 1. Effect of metal composition of LDHs on phosphate adsorption from sewage sludge filtrate. M(II)/M(III) molar ratio of 2 was used to prepare these LDHs.

3.1.2. Zn/Al molar ratio

In order to investigate the effect of Zn/Al molar ratio on phosphate uptake, five different Zn–Al LDHs were used in adsorption assays. A Zn/Al ratio of 2 appeared optimal for phosphate adsorption by LDHs; more Zn^{2+} replacement by Al^{3+} (e.g. Zn/Al of 1:1 or 1:2) decreased the adsorption capacity instead of further improvement (Fig. 2). Optimal results for other metal combinations have been reported elsewhere: Mg/Al of 2:1 [19], Mg/Mn of 3:1 [21] and Ni/Al of 3:1 [24]. Phosphate adsorption activity of LDHs compounds results from the positively charged hydroxylated sheet, which is developed by partial substitution of trivalent for divalent cations. In this study, introduction of more Al^{3+} would improve the net positive charge of the mixed metal hydroxide layers and subsequently the phosphate adsorption. On the other hand, this may also lead to disorder of the layered hydrotalcite-like structure of LDHs or even phase change due to the radius difference between Zn and Al, and cause the decrease in phosphate uptake [25].

3.1.3. Calcination

Calcined products of Zn–Al LDHs (CLDHs) generally had a higher adsorption capability as shown in Fig. 3. The greatest phosphate uptake (40.77 mg P/g) was observed when the adsorbent was calcinated at 300°C . The adsorption was 1.55-fold higher than that of the uncalcined material. Beyond this temperature, the adsorption

Fig. 2. Effect of Zn/Al molar ratio on phosphate adsorption from sewage sludge filtrate.

Fig. 3. Effect of calcination temperature on phosphate adsorption by LDHs from sewage sludge filtrate.

capacity of CLDHs went down slightly, with a sharp decrease after calcination at 600 °C. The improvement in adsorption of anions by LDHs calcination has also been addressed previously. For example, Mandal and Mayadevi reported that the fluoride uptake was increased by 21.2% after calcination of the Zn–Al LDHs at 450–500 °C [26]. Carja et al. found that calcination (450 °C) markedly increased the removal efficiency of As(V) oxyanions up to >90% for all the Fe-containing LDHs tested [27].

Some thermally decomposed LDHs will undergo spontaneous rehydration and structural reconstruction, called “Memory Effect”, when added to an aqueous medium [28]. Anion incorporation occurs simultaneously in this process, increasing the anionic exchange capacity of this compound [29]. XRD pattern indicates that the LDHs phase completely disappeared and was replaced by phases of metal oxides after calcination at 300 °C for 4 h (Fig. 4). The result is in accordance with that of TG–DSC analysis (data not shown), in which the first stage of mass loss of ~17% was observed with the temperature increasing to 300 °C. This phase transformation was obviously responsible for the marked increase in phosphate adsorption by CLDHs for the following three reasons: (1) a higher surface area was obtained in calcined particles, (2)

Fig. 4. XRD patterns of Zn–Al–2, Zn–Al–2–300, and Zn–Al–2–300 after phosphate adsorption.

Fig. 5. Effect of pH on phosphate adsorption by Zn–Al–2–300 from sewage sludge filtrate. The inset shows a buffer effect by the LDHs addition.

obstacle anions (mainly CO_3^{2-}) were released from the precursor, producing more active sites for phosphate adsorption and (3) phosphate incorporation occurred during the LDHs reconstruction. However, a higher calcination temperature did not lead to further improvement in phosphate uptake. It can be explained by the fact that a mixture of ZnO and spinel-type ZnAl_2O_4 was formed under high temperatures instead of a metastable phase in the first stage, only which may reconstruct under appropriate conditions (Fig. 4). In addition, the specific surface area started to decline because of sintering when the temperature went beyond 300 °C (data not shown), which would have weakened the surface adsorption. The used Zn–Al–2–300 had the same type of XRD pattern with the uncalcined Zn–Al LDHs indicating the layered structure was recovered after adsorbing phosphate from the sludge filtrate (Fig. 4). However, the crystallinity was lowered attested by the broadening of the diffraction peaks and the decrease in their intensity. This may be due to the high impurity in the waste stream.

3.1.4. pH

pH of a solution generally plays an important role in the physicochemical reaction at the water–solid interface. In addition, phosphate dissociation equilibria in liquid are pH-related, which can be presented as [30]:

where $\text{p}K_1 = 2.15$, $\text{p}K_2 = 7.20$ and $\text{p}K_3 = 12.33$, respectively. In Fig. 5, a buffer effect of pH and LDHs dissolution were observed under acidic and highly alkaline conditions due to the amphoteric character of aluminum hydroxide. An acidic environment with a pH below 5 adversely affected phosphate uptake by the adsorbent due to the significant LDH dissolution as indicated by a sharp increase of Zn^{2+} in bulk water. Increased phosphate removal at pH 5, however, was attributed to a coagulation process with Al^{3+} ions from partial dissolution of the LDHs compound.

High adsorption capacity of ~30 mg P/g was achieved when the pH of the solution was above 8. A slight decrease in the adsorption capacity of the LDHs occurred in the circumneutral environment possibly resulting from the weakening of its electrostatic interaction with phosphate, which transformed from a divalent to a monovalent ion. Based on these results it appears that Zn–Al–2–300 could be used as an effective adsorbent for phosphate recovery from sewage sludge filtrate and other phosphate-rich effluents with pHs ranging from 5 to 10.

Fig. 6. Kinetics of phosphate adsorption on Zn-Al-2-300 from sewage sludge filtrate and data fitting by pseudo-first-order, pseudo-second-order and Elovich models.

3.2. Adsorption kinetics

According to Fig. 6, the majority of phosphate adsorption from sludge filtrate was completed in 24 h. The phosphate adsorption capacity of Zn-Al-2-300 at equilibrium could be obtained in approximately 72 h and is estimated to be 50 mg P/g. The kinetics data were analyzed using pseudo-first-order, [35] pseudo-second-order [36] and Elovich models [37] (Fig. 6). Though a high correlation coefficient ($R^2 > 0.9$) is obtained in each model, the phosphate adsorption in the present study most closely followed pseudo-second-order kinetics, by which a very accurate estimation of q_e is achieved as well as the highest correlation coefficient ($R^2 > 0.99$) (Table 3). Comparable results were observed in phosphate adsorption onto ZnCl₂ activated coir pith carbon [31], calcined electrocoagulated metal hydroxides sludge [32], amorphous zirconium hydroxide [14] and dolomite [33].

3.3. Adsorption isotherm

Adsorption isotherms of phosphate on Zn-Al CLDHs at different temperatures are presented in Fig. 7. At the same equilibrium concentration of phosphate in the sludge filtrate, the adsorption capacity of the LDHs increased with an increase in water temperature in the range from 25 to 30 °C. However, in the 50 °C test the adsorption capacity approximated that found in the 25 °C test. This

Fig. 7. Isotherms of phosphate adsorption on Zn-Al-2-300 from sewage sludge filtrate and KH₂PO₄ solution. The KH₂PO₄ solutions had the same phosphorus concentration as in the sludge filtrate: 20 mg P/L.

result may be due to the microorganisms existing in the sludge filtrate, which could have exhibited higher activity and consumed a portion of phosphate under a mesothermal environment, therefore lowering the contribution of adsorption in phosphate removal. In

Table 3
Kinetic models for phosphate adsorption on calcined Zn-Al LDHs from sludge filtrate and the calculated constants.

Model	Equation	Simplified form	Constant	R ²
Pseudo-first-order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1}{2.303} t$	$q_e = 34.6, k_1 = 0.165$	0.945
Pseudo-second-order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$q_e = 50.0, k_2 = 0.00913$	0.997
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$	$\alpha = 113, \beta = 0.142$	0.976

^a q_e and q_t are the phosphate uptake (mg P/L) at equilibrium and at time t (h), respectively. k_1 is the Lagergren rate constant of pseudo-first-order adsorption (h⁻¹), k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg h), α and β are constants of Elovich equation.
^bConstants in pseudo-second-order and Elovich equation were calculated without using q_0 ($t = 0, q_0 = 0$).

KH_2PO_4 solutions, only a clear improvement in phosphate uptake at equilibrium was observed with the gradual temperature increase. These results revealed that phosphate adsorption is an endothermic process. Furthermore, the significantly higher adsorption capacity obtained when using pure phosphate solutions, compared with that in sludge filtrate tests, at temperatures beyond 30°C demonstrated the enhancement of biological activity in the sludge filtrate.

Langmuir and Freundlich models were introduced to study the adsorption isotherms. The linear form of the Langmuir equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where C_e (mg/L) is the phosphate concentration at equilibrium, q_e (mg/L) the corresponding adsorption capacity, q_m (mg/g) the maximum adsorption capacity and b (L/mg) the affinity coefficient [31]. The essential characteristics of the Langmuir model can be described by a dimensionless constant called the equilibrium parameter R_L ,

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where C_0 is the initial concentration of phosphate in solutions. The logarithmic form of Freundlich equation is represented as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where q_e (mg/g) is the corresponding adsorption capacity, C_e (mg/L) the phosphate concentration at equilibrium, K_f and n are constants.

The results of fitting the experimental data to the two models are presented in Table 4. The Langmuir model clearly exhibits a better fit for phosphate adsorption on the calcined LDHs compared to the Freundlich model. In assays of both pure KH_2PO_4 solution and sludge filtrate, very high correlation coefficients ($R^2 > 0.99$) were observed when using the Langmuir model.

3.4. Phosphate desorption and LDHs regeneration

Assays of phosphate desorption were conducted using three types of solutions as shown in Table 2. NaCl solution was not suitable for exchanging PO_4^{3-} from P-loaded Zn–Al LDHs even at high concentration (20 wt%) when compared with the other two desorption solutions. Kuzawa et al. [13] used 30 wt% NaCl solution to elute phosphate from granular Mg–Al LDHs and the desorption rate was even lower (14%). These results were expected due to the relatively low affinity of Cl^- with LDHs compounds [21]. More than 80% of the phosphate on the LDHs can be desorbed by NaOH or NaCO_3 solution with concentrations of 5 wt% and 10 wt%, respectively. Unfortunately, carbonate anion acts as an obstacle to phosphate uptake by LDHs because of its high selectivity [34].

Table 4

Langmuir and Freundlich constants for phosphate adsorption on calcined Zn–Al LDHs from sewage sludge filtrate.

Temp. ($^\circ\text{C}$)	Langmuir equation				Freundlich equation		
	$q_{\max}$	b	R_L	R^2	K_f	n	R^2
<i>Sludge filtrate (initial phosphate concentration: around 20 mg/L)</i>							
25	35.81	13.64	0.003450	1.0000	28.32	6.436	0.8461
30	44.11	6.495	0.006947	0.9998	32.48	4.658	0.8796
40	47.82	3.114	0.01580	0.9988	30.08	4.239	0.9340
50	35.73	12.77	0.004855	0.9955	27.11	4.606	0.7928
<i>KH_2PO_4 solution (initial phosphate concentration: 20 mg/L)</i>							
25	35.85	3.094	0.01590	0.9988	23.79	6.490	0.9123
30	58.22	3.993	0.01237	0.9980	40.28	6.362	0.9250
40	79.08	6.962	0.007131	0.9993	55.14	4.980	0.9293
50	92.58	4.250	0.01163	0.9972	58.37	4.059	0.8632

Fig. 8. Recovery, desorption and regeneration rates of Zn–Al–2–300 in the cycle assays.

Therefore, using NaCO_3 in the desorption step introduces a challenge to the regeneration of the used LDHs. On the other hand, CO_3^{2-} in the desorption solution makes it impossible to recover the enriched phosphorus as calcium phosphate. A higher desorption rate of phosphate was achieved with an increasing concentration of NaOH solution as the desorbent, however, LDHs dissolution can not be overlooked at NaOH concentrations beyond 5 wt%, as indicated by the elevated levels of metal cations in the liquid phase (Table 2). No previous research has as yet addressed this phenomenon; however, the stability and activity of Al-containing LDHs compounds in each step of phosphate adsorption/recovery need further investigation.

A series of seven cycles of adsorption, desorption and regeneration were conducted to estimate the reusability of Zn–Al–2–300 during phosphate recovery from sewage sludge filtrate. Fig. 8 illustrates that the rates of LDHs particle recovery and phosphate desorption remained above 80% throughout seven cycles of operation. The regeneration rate was approximately 60% after six cycles indicating the accumulation of some interfering substance. The expiration of LDHs seemed slightly faster than in other studies (e.g., regeneration rate of almost 80% after six cycles [13]). This is probably due to larger quantities of impurities and coexisting ions contained in the real sludge filtrate vs. that found in pure phosphate solutions, which interfered with phosphate adsorption by binding a portion of the active sites on the LDHs.

4. Conclusions

Magnetic particles of layered double hydroxides were used in this study in order to separate and recover phosphate from sludge filtrate from Taiping municipal wastewater treatment plant in Harbin, China. Zn–Al LDHs with Zn/Al molar ratio of 2 was found to be more efficient for phosphate adsorption in comparison to the other LDHs synthesized. Calcination remarkably improved phosphate adsorption by Zn–Al–2 because of the phosphate incorporation which occurred in the spontaneous rehydration and structural reconstruction of the calcined LDHs. After calcination at 300°C for 4 h, a phosphate adsorption capacity of 40.77 mg P/g adsorbent was achieved. An acidic or highly alkaline environment adversely affected phosphate adsorption by Zn–Al–2–300 since aluminum hydroxide is amphoteric. Kinetics of phosphate adsorption from sewage sludge filtrate in this study followed a pseudo-second-order model. Adsorption isotherms indicated that

phosphate uptake by Zn–Al-2-300 was an endothermic process and fitted the Langmuir model well. Phosphate desorption from LDHs particles can be effectively realized by using 5 wt% of NaOH solution, and a regeneration rate of ~60% was observed after six operation cycles. Thus, despite of the complexity of the micro-process involved, phosphate adsorption and recovery from sewage sludge filtrate by using optimized layered double hydroxides appears to be a promising nutrient removal technology.

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