



Enhanced adsorption removal of phosphate from water by mixed lanthanum/aluminum pillared montmorillonite

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ABSTRACT

In order to explore the feasibility of improving phosphate adsorption ability of aluminum pillared clays (Al-PILCs) by doping with lanthanum, mixed lanthanum/aluminum pillared clays (LaAl-PILCs) were prepared and investigated for their ability to remove phosphate from water. The structures of LaAl-PILC and Al-PILC were confirmed by XRD characterization. The applicability of adsorption models for the present isotherms approximately followed the order: Freundlich > Langmuir > Temkin. As the isotherms indicated, LaAl-PILC has a phosphate adsorption capacity of about 1.3 times the value of Al-PILC. The thermodynamic analysis indicated that the adsorption process was spontaneous and exothermic in nature. Pseudo-first-order kinetic equation can provide satisfactory fitting of the kinetic data. The pseudo-first-order kinetic constant (k_1) of LaAl-PILC, 1.0086 h^{-1} , is much greater than that of Al-PILC, 0.4369 h^{-1} . The phosphate adsorption on the PILCs tends to increase with a decrease of pH, maximum adsorption occurred at around pH <5.0 and <4.0 for LaAl-PILC and Al-PILC, respectively. The concomitant anions have profounder adverse effect on phosphate adsorption of LaAl-PILC than on that of Al-PILC and the effects follow the order: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} \approx \text{NO}_3^-$. The concentration of lanthanum released from LaAl-PILC decreased gradually with the increase in pH and cannot be detected at pH higher than 4.5. LaAl-PILC was successfully tested as an adsorbent for the removal of phosphate from a contaminated water samples containing phosphate produced in process of yellow phosphorus and regenerated for reuse by removing the adsorbed phosphate with NaOH. The present study confirmed that LaAl-PILC would be one of candidates for phosphate adsorbent.

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1. Introduction

The presence of trace concentration of dissolved phosphate in the treated wastewater from municipalities and industries is often responsible for causing eutrophication problems [1,2]. The treatment technologies presently available for phosphorus removal include: (i) biological treatment, (ii) chemical precipitation, (iii) crystallization, (iv) tertiary filtration, (v) ion exchange and (vi) adsorption [2–4]. Most of these approaches are generally more suitable for the removal of phosphate of higher concentration. The removal of phosphate of lower concentration is relatively difficult. Adsorption is recommended as one of the most effective removal processes for the low concentrations of phosphorus. Many types of adsorbents for phosphate removal have been investigated, which include aluminum oxide hydroxide [5], aluminum oxides [6], poly-

meric ligand exchanger [1,7], iron oxides [8,9], aluminum salts [10], dolomite [11], zeolite [12], gas concrete [13], mesoporous silicates [14] and so on.

In contaminated/wastewater processes, natural minerals are usually used as adsorbents and have attracted much attention for their higher removal efficiency, lower cost and variety of properties [15–18]. Montmorillonite, one of the most abundant clay minerals at the earth surface, was also found to be an effective adsorbent for the removal of toxic compounds from soil, water, and air [18]. The most effective minerals for phosphate adsorption are Al-bearing minerals which have Al–OH and Fe–OH functional groups on the mineral surface [19]. Montmorillonite show higher affinity to cations but hardly uptake anions such as phosphates for its characteristics of permanent negative charge and less amount of reactive sites such as Al–OH [19].

Exchanging the interlayer cations of the layered clay minerals such as montmorillonite for other inorganic species originates pillared interlayered clays (or pillared clays, PILCs). PILCs are typically synthesized by exchanging the interlayer cations of clay with so-called pillaring agent, large oligomeric polycations such as the Keggin-like Al_{13} oligomer $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The synthesis and characterizations of PILCs have been carried out by a number

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of authors and PILCs are extensively studied as adsorbents and as catalysts [20,21]. PILCs show higher affinity to cations (such as Cd, Cu, Zn, and Ni), anions (such as phosphate) and organics in water than nonpillared clay because of the presence of Al–OH and Al–H₂O [19,22–27]. Recently, the use of PILCs, especially Al–PILC, to remove phosphate in wastewater has attracted much attention.

For the various purposes, PILCs can be prepared with different polycationic species or introduced mixed pillars into the materials. In principle, any metal (e.g. zirconium, titanium, chromium, and iron) oxide or salt that forms polynuclear species upon hydrolysis can be inserted as pillars [28,29]. In order to intensify the phosphate adsorption onto PILCs, one potential way is to introduce mixed pillars into the materials. Rare earth, typical lanthanum, was usually used to modify adsorbents for the removal of anions (P, F) from water, and showed high-adsorption capacity for phosphate removal [7,30–32]. Since lanthanum exhibited more adsorptive capability for phosphate, and suitable lanthanum may be nontoxic and environment friendly, a good possibility to apply mixed lanthanum/aluminum pillared clays (LaAl–PILCs) for the phosphate removal was suggested.

Mixed PILCs such as LaAl–PILC have been synthesized and characterized by a number of authors [33–39]. According to our literature survey, there have been considerable works reported on the adsorption of phosphate from water by Al–PILC, however, LaAl–PILCs have not been used as adsorbent for phosphate removal previously. In this study, two PILCs, one pillared with lanthanum/aluminum (LaAl–PILC) and the other pillared only with aluminum (Al–PILC) were prepared and used for the removal of phosphate from water. The structure characteristics were investigated through characterization with X-ray diffraction (XRD). The adsorption isotherms, kinetics and thermodynamics of phosphate adsorption on LaAl–PILC and Al–PILC were examined and compared. The influences of pH, temperature and common concomitant anions in natural water on adsorption of phosphate on LaAl- and Al–PILCs were determined. The desorption amounts of lanthanum from LaAl–PILC under various conditions of pH were also investigated. The LaAl–PILC would be tested as an adsorbent for the removal of phosphate from a contaminated water samples containing phosphate.

2. Methods and materials

2.1. Materials

The natural bentonite used, which consists mainly of Ca²⁺-montmorillonite, was obtained from Inner Mongolia, China. The bentonite has a CEC of 108 mequiv./100 g and the structural formula calculated from chemical analysis and CEC measurements is: Na_{0.017}K_{0.02}Ca_{0.39} [Fe_{0.17}Mg_{0.55}Al_{1.26}Ti_{0.02}]₂-[Si_{3.96}Al_{0.04}]₄O₁₀(OH)₂·5.49H₂O. The clay sample was ground and the fraction which can pass a 100 mesh sieve was used in this study. LaCl₃·7H₂O, AlCl₃·6H₂O, Na₂CO₃, NaOH, HCl, NaHCO₃, NaCl, NaNO₃, Na₂SO₄, KH₂PO₄, ascorbic acid, arsenazo(III), ammonium molybdate and antimony potassium tartrate were of analytical grade, obtained from Shanghai Chemical Co., China. All reagents were used as received.

2.2. Preparation and characterization of PILCs

Al–PILC was synthesized according to the following procedure [40]. Under stirring, 6 L of a 1 mol/L Na₂CO₃ aqueous solution was added dropwise to 10 L of a 0.5 mol/L AlCl₃·6H₂O aqueous solution at the temperature of 60 °C to obtain a molar ratio [OH⁻]/[Al³⁺] = 2.4. The pillaring solution was stirred for another 2 h and aged overnight at room temperature. Under vigorous stirring, 500 g of bentonite was dispersed into the pillaring solution at 60 °C. The mixture

was stirred continuously for 5 h at the same temperature and then cooled to room temperature. After 24 h, it was separated by filtration and washed with distilled water for four times. The solid was oven-dried at 110 °C for 24 h and sequentially vacuum-desiccated at 105 °C for 24 h. The dried product is dominated as Al–PILC.

Besides the pillaring solution was prepared according the following steps, the synthesis procedure of LaAl–PILC was the same as that of Al–PILC. A solution of 0.1 mol/L LaCl₃ in 500 mL of water was mixed with 500 mL of a 0.1 mol/L AlCl₃ aqueous solution. Under stirring, 1.2 L of a 0.1 mol/L NaOH aqueous solution was added dropwise to the mixed solution at 60 °C. The solution was stirred for another 5 h, precipitated for 72 h, aged for 10 h at 90 °C. Finally, a mixed pillaring solution of lanthanum and aluminum was obtained.

XRD patterns were recorded on a Rigaku D/max-2550PC diffractometer using Cu K α radiation under 40 kV, 300 mA current intensity in the 2 θ 0.5–30° range at 4°(2 θ)/min. Basal spacings were determined by X-ray diffraction from the position of the 001 peak.

2.3. Phosphate adsorption experiments

For the equilibrium experiments, a fixed mass of adsorbent was added into a conical flask with 50 mL of phosphate solution in various initial concentrations. The solution of phosphates was obtained by dissolving potassium dihydrogen phosphate (KH₂PO₄) in deionized water. The initial pH of the solution was adjusted to 5.0 with 1 mol/L HCl and/or 1 mol/L NaOH. The sealed flasks were then put in a shaker bath at various constant temperatures (\pm 0.5 °C) for 12 h, shaken at the 170 rpm. Following adsorption, the suspension was filtered by using a membrane filter of 0.45 μ m and the filtrates were analyzed for phosphate concentration. The equilibrium adsorption capacity was calculated by the equation: $Q = V(C_0 - C_e)/m$, where Q is the adsorption capacity (mgP/g), V is the volume of solution (mL), C_0 is the initial concentration of phosphate (mgP/L), C_e is the equilibrium concentration (mgP/L), and m is the weight of adsorbent (g). In order to determine the effect of temperature on adsorption, isotherms were established at 25, 30 and 35 °C.

Adsorption experiments for the kinetic study were conducted as follow: 0.1 g of each adsorbent was suspended in 40 mL solution containing 10 mgP/L of phosphate. The solution pH was adjusted to 5.0 with 1 mol/L HCl and/or 1 mol/L NaOH. The sealed flasks were then put in a shaker bath at 25 \pm 0.5 °C, shaken at the 170 rpm for different time intervals. The flasks were taken out at various times for the analysis of phosphate concentrations. The rate of phosphate adsorption was determined from the amount of phosphate adsorbed at various times.

To evaluate the effect of pH on phosphate adsorption, experiments were performed at various initial pH, ranging between 3.0 and 8.0. Initial phosphate concentration of 5 mgP/L and 2.5 g of sorbent per liter of solution were used. The suspensions were shaken for 12 h at 25 \pm 0.5 °C.

To determine the effect of concomitant anions on adsorption of phosphate, various anions, HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻, were added into phosphate solutions in the sodium form. The concentrations of the anions in these experiments were all 0.5 mmol/L, corresponding to those in natural fresh water. Initial phosphate concentration of 5 mgP/L and 2.5 g of sorbent per liter of solution were used. The initial pH of the solution was adjusted to 5.0. The suspensions were shaken for 12 h at 25 \pm 0.5 °C.

To evaluate the stability of lanthanum pillared into LaAl–PILC at adsorption process, 0.1 g of LaAl–PILC was added to six conical flasks with 50 mL of deionized water. The solution pH of each conical flask was then adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0, respectively. After being shaken at 25 \pm 0.5 °C, 170 rpm in a shaker, the suspension solutions were filtered and analyzed for the desorbed lanthanum.

Concentration of phosphate was determined spectrophotometrically with a UV–vis spectrophotometry of UV–2450PC (Shimadzu,

Japan) at 700 nm, following the ascorbic acid method [41]. The concentration of lanthanum was determined by means of spectrophotometric method, with arsenazo III as a developer at 660 nm [42].

2.4. Regeneration experiment

For regeneration studies, 2.5 g/L of LaAl-PILC was dispersed in phosphate solution as mentioned in the equilibrium experiments. The phosphate saturated adsorbent was separated by using a membrane filter of 0.45 μm . The obtained solid was immersed for 12 h with the 0.1 M NaOH solution to desorb the phosphate. The phosphate adsorption capacity was determined by following the same procedure described above section.

2.5. Experiment for removing phosphate from real wastewater

The wastewater was obtained from a yellow phosphorus factory (Jianglin Group Co. Ltd., Yunnan, China). The main pollutants in the wastewater are as follows: dissolved phosphate (43.65 mgP/L), F^- (55.8 mg/L), As (0.015 mg/L), COD (45.60 mg/L) and SS (11 mg/L). Initial pH of the wastewater was 6.0. Prior to the adsorption experiment, pH was adjusted to various values as required with 1 mol/L HCl. In order to compare with the synthetic phosphate solution, the phosphate concentration of wastewater was diluted to 5 mgP/L. The phosphate adsorption capacity was determined according to the procedure described in the experiment for the effect of pH on phosphate adsorption.

3. Results and discussion

3.1. Structure characterization

The XRD patterns for LaAl-PILC and Al-PILC are presented in Fig. 1. As a reference, the diffraction pattern of the raw montmorillonite is shown as well. The montmorillonite sample shows a diffraction peak at $2\theta = 5.78^\circ$, which corresponds to a basal spacing of 1.53 nm. Taking into account the thickness of a montmorillonite clay layer equal to 0.96 nm, an interlayer spacing for montmorillonite sample is equal to 0.57 nm. For Al-PILC with a diffraction peak at $2\theta = 4.40^\circ$, the basal spacing is 2.01 nm and the interlayer spacing is 1.05 nm. This peak associates with the basal spacing d_{001} between

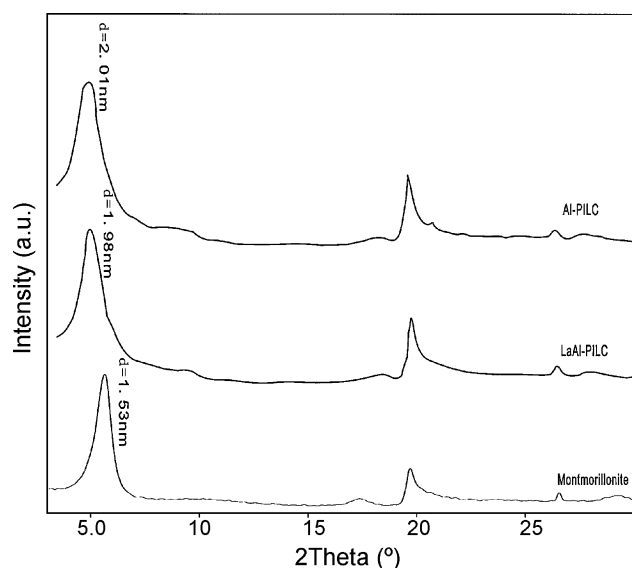


Fig. 1. X-ray diffraction patterns for PILCs and montmorillonite.

the clay layers and characteristics of clays pillared with aluminum polyoxycation (Keggin ion) and is in agreement with the expected values described in the literature [39]. The diffraction peak for LaAl-PILC at $2\theta = 4.46^\circ$ corresponds to a basal spacing of 1.98 nm and the free spacing between the clay sheets is 1.02 nm, which is the difference between the basal spacing and the thickness of a single sheet of montmorillonite clay (0.96 nm). The basal spacings of LaAl-PILC, 1.98 nm, are significantly larger than the basal spacings of montmorillonite and slightly larger than those reported by previous studies, 1.80–1.87 nm [38]. By the comparison of the basal spacings between the Ca and LaAl-PILC samples, it was confirmed that the La/Al pillars were formed in the interlayers of the LaAl-PILC samples [19]. After intercalation, the $d(001)$ basal spacing increased considerably up to 2.01 nm for Al-PILC, 1.98 nm for LaAl-PILC in comparison with the precursor material, which presented only 1.53 nm for Ca-montmorillonite. As can be seen from the shift of the characteristic peak corresponding to d_{001} spacing, it is evident that some pillaring has taken place.

3.2. Adsorption isotherms

Phosphate adsorption isotherms for 25, 30 and 35 $^\circ\text{C}$ were obtained at pH 5.0 by varying the initial concentration of phosphate (2.5–50 mgP/L). The isotherms of phosphate on LaAl-PILC and Al-PILC are shown in Fig. 2. The phosphate adsorption capacity considerably increased with the phosphate equilibrium concentration increasing from 0 to 20 mgP/L. The isotherms show that the doping of lanthanum can remarkably improve the phosphate adsorption of PILCs. For example, at an equilibrium concentration of 25 mgP/L and temperature of 25 $^\circ\text{C}$, the adsorption capacity of phosphate on LaAl-PILC is 8.90 mgP/g, and is 1.33 times the value of Al-PILC, 6.67 mgP/g.

The isotherm data from Fig. 2 were fitted to three well-known models described below in Eqs. (1)–(3) by non-linear regression using the method of least squares [43]:

$$\text{Freundlich equation } Q_e = K_F C_e^{1/n} \quad (1)$$

$$\text{Langmuir equation } Q_e = Q_m K_L \frac{C_e}{1 + K_L C_e} \quad (2)$$

$$\text{Termkin equation } Q_e = A + B \ln C_e \quad (3)$$

where Q_e is the equilibrium adsorption capacity (mgP/g); C_e is the equilibrium concentration of phosphate in aqueous phase (mgP/L); Q_m is the maximum adsorption capacity (mgP/g); K_F and n are Freundlich constants; K_L is Langmuir constant (L/mg); A and B are Termkin constants. The curve fitting and statistical analyses were performed with OriginPro 7.0 software. The estimated model parameters with the correlation coefficient (R^2) for the different models are shown in Table 1. The correlation coefficients, R^2 , given in the Table 2 also show that the isotherms of both LaAl-PILC and Al-PILC can be satisfactorily described by both Freundlich and Langmuir equations. In terms of R^2 values, the applicability of the three above models for the present experimental data approximately follows the order: Freundlich > Langmuir > Temkin. Kuroda et al. [5] reported that the isotherms of phosphate adsorption onto many adsorbents fit the Freundlich equation. The isotherm of phosphate adsorption onto aluminum oxide hydroxide [5] and Al-PILC [22] followed to the Freundlich equation. Ding et al. [31] suggested that the isotherm of phosphate adsorption on lanthanum hydrate can be well fitted with Langmuir equation. These results show reasonably good agreement with the observations of previous reports on the adsorption of phosphate onto the other Al-related adsorbents.

In Freundlich equation, K_F and $1/n$ are the constants related to adsorption capacity and intensity of adsorption, respectively. K_F values for LaAl-PILC (1.722, 1.054 and 0.773 at 25, 30 and 35 $^\circ\text{C}$, respectively) are larger than those for Al-PILC (1.210, 0.765 and

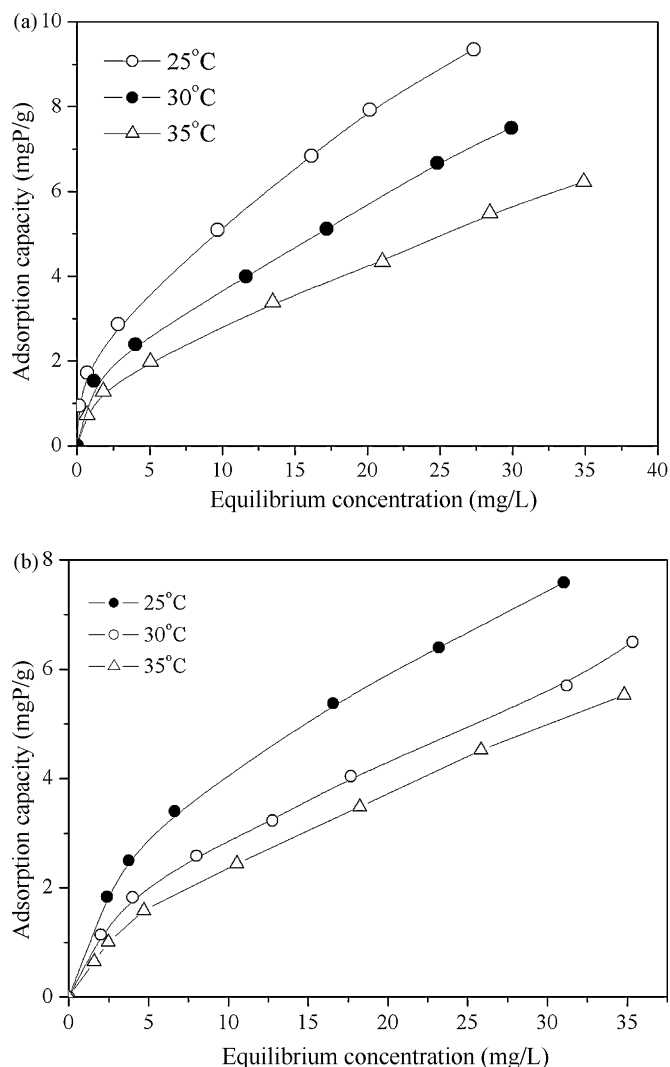


Fig. 2. Isotherms of phosphate on LaAl-PILC (a) and Al-PILC (b).

Table 1
Estimated isotherm parameters for phosphate adsorption on LaAl-PILC and Al-PILC.

Sample	Temperature (°C)	Freundlich equation $Q_e = K_f C_e^{1/n}$			Langmuir equation $Q_e = Q_m K_L C_e / (1 + K_L C_e)$			Termkin equation $Q_e = A + B \ln C_e$		
		K_f	$1/n$	R^2	Q_m (mgP/g)	K_L (L/mg)	R^2	A	B	R^2
LaAl-PILC	25	1.722	0.505	0.9942	13.022	0.078	0.9681	2.707	1.355	0.9180
	30	1.054	0.570	0.9930	12.297	0.047	0.9700	0.551	1.777	0.9335
	35	0.773	0.581	0.9968	9.839	0.044	0.9738	0.567	1.350	0.9314
Al-PILC	25	1.210	0.533	0.9994	10.307	0.076	0.9910	-0.386	2.1825	0.9868
	30	0.765	0.581	0.9985	8.978	0.050	0.9833	-0.332	1.575	0.9594
	35	0.536	0.652	0.9981	7.902	0.047	0.9900	-0.222	1.313	0.9655

Table 2
Comparison of phosphate adsorption capacities of various adsorbents.

Adsorbent	pH	Initial concentration of phosphate (mgP/L)	Phosphate adsorption capacity (mgP/g)	Data source
Montmorillonite	7.6	3.5–25	0.746	[16]
Kaolinite	7–8	3.4–40	0.091	[16]
Illite	7.5	10–30	2.51	[16]
Al-PILC	3–4	99.2	20.46–26.97	[19]
Al-PILC	5.5	No data	7.10	[23]
La(III)-chelex resin	5.5	155	3.038	[7]
La(III)-modified zeolite	6.0	No data	24.6	[44]
Calcined Mg-Al-LDHs	6.0	50	44	[45]
Dry iron oxide tailings	3.5	10	8	[9]

0.536 at 25, 30 and 35 °C, respectively). K_f values of both PILCs decrease with the increasing of temperature. According as K_f values, LaAl-PILC has a larger adsorption capacity of phosphate than Al-PILC, and the adsorption capacities of phosphate decrease with the increasing of temperature for both PILCs. $1/n$ values for between 0 and 1 represent good adsorption of phosphate on PILCs. $1/n$ values imply also that the interaction between the LaAl-PILC and phosphate was greater than that between the Al-PILC and phosphate.

In Langmuir equation, the decrease in the value of Q_m with increasing temperature means a decrease in adsorption capacity of the adsorbent for phosphate on both PILCs and exothermic nature of the adsorption process. Decreasing values of K_L with temperature are accompanied by low-energy requirement for phosphate adsorption onto both PILCs.

The values of Q_m for LaAl-PILC are 1.26, 1.37 and 1.25 times that values for Al-PILC at 25, 30 and 35 °C, respectively. As indicated by values of Q_m , LaAl-PILC has higher adsorption capacities for phosphate than Al-PILC. It is clear that the doping of lanthanum can enhance significantly the phosphate adsorption.

For comparison, the phosphate adsorption capacities of other common adsorbents given in Table 2. Because of the differences of experimental conditions such as initial phosphate concentrations, pH and concomitant anions, the adsorption capacities of various adsorbents is not strictly comparable. It was found, in general, that the adsorption capacities of LaAl-PILC at various temperatures (as indicated by Q_m values in Table 1, 9.839–13.022) is not most prominent. The adsorption capacities of LaAl-PILC is even lower than La(III)-modified zeolite and calcined Mg-Al-LDHs but higher than the values of several common clays (montmorillonite, kaolinite and illite), La(III)-chelex resin and dry iron oxide tailings which are regarded as effective adsorbents to remove phosphate from water. It must be noticeable that differences in the reported adsorption capacities of Al-PILCs obviously may be due to the properties of original clays and the preparing procedures. The adsorption capacities of Al-PILC in this study (as indicated by Q_m values in Table 1, 7.902–10.307) are nearly consistent with the value reported in reference [23], but far from that reported in reference [19]. This result implies that the adoption of various original clays and preparing procedures may ulteriorly improve the adsorption capacity of LaAl-PILC.

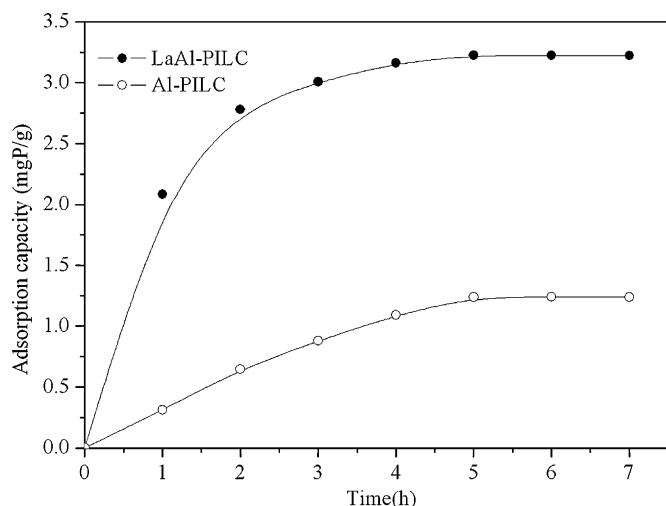


Fig. 3. Adsorption kinetics of phosphate on PILCs.

3.3. Phosphate adsorption kinetics

The initial experiments of this investigation were kinetic in nature for the purpose of determining the reaction time required for the phosphate adsorption reaction to reach equilibrium. These experiments were conducted under the following conditions: initial phosphate concentration of 6.54 mgP/L, pH 5.0, temperature of 25 °C and adsorbent dose of 2.5 g/L. The kinetic results are shown in Fig. 3 and show that the adsorption of phosphate onto PILCs is comparatively faster and attains equilibrium at about 5 h. Further increase in retention time does not seem to have any impact on the equilibrium concentration. This is in agreement with the work of the other investigators [16] who proposed that the phosphate-clay adsorption reaction is rapid with equilibrium being reached within 4–8 h.

The phosphate adsorption kinetic data were fitted with the pseudo-first-, pseudo-second- and pseudo-third-order kinetic models by non-linear regression using SigmaPlot 10.0 software. The kinetic equations can be written as follows [43]:

$$C_t = C_0 - (C_0 - C_e)(1 - e^{-k_1 t}) \quad (4)$$

$$C_t = C_0 - (C_0 - C_e) \left(1 - \frac{1}{1 + k_2 t} \right) \quad (5)$$

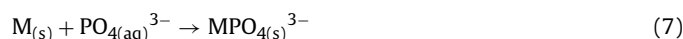
$$C_t = C_0 - (C_0 - C_e) \left(1 - \frac{1}{(1 + 2k_3 t)^{1/2}} \right) \quad (6)$$

where t is the time (h); C_t is the initial phosphate concentration (mgP/L); C_t is the phosphate concentration at time t (mgP/L); C_e is the equilibrium phosphate concentration (mgP/L); k_1 , k_2 and k_3 are adsorption rate constants for the pseudo-first-, pseudo-second- and pseudo-third-order models, respectively (h^{-1}). The used kinetic equations and acquired parameters with R^2 are summarized in Table 3. With respect to the correlation coefficient, R^2 , the pseudo-first-order model could adequately describe the adsorption kinetics for both PILCs. This high applicability of the pseudo-first-order kinetic equation for the present kinetic data is generally in agreement with other researchers' results that the pseudo-first-order kinetic equation was able to properly describe the adsorption kinetics of phosphate on lanthanum hydrate [31], aluminum oxide hydroxide [5], aluminum oxide and kaolinite [6]. The high-determination coefficients (R^2) for a pseudo-first-order kinetic equation for both PILCs implied that one adsorbate (PO_4^{3-}) may be adsorbed onto one surface site of PILCs, the chemical equa-

Table 3
Kinetic parameters for phosphate adsorption on PILCs.

	Pseudo-first-order kinetic model	
	$C_t = C_0 - (C_0 - C_e)(1 - e^{-k_1 t})$	
	k_1	R^2
LaAl-PILC	1.0086	0.9993
Al-PILC	0.4369	0.9602
	Pseudo-second-order kinetic model	
	$C_t = C_0 - (C_0 - C_e) \left(1 - \frac{1}{1 + k_2 t} \right)$	
	k_2	R^2
LaAl-PILC	2.7897	0.9728
Al-PILC	0.8269	0.8551
	Pseudo-third-order kinetic model	
	$C_t = C_0 - (C_0 - C_e) \left(1 - \frac{1}{(1 + 2k_3 t)^{1/2}} \right)$	
	k_3	R^2
LaAl-PILC	12.0466	0.9392
Al-PILC	1.6785	0.7641

tion is [43]



The pseudo-first-order kinetic constant (k_1) of LaAl-PILC, 1.0086 h^{-1} , is much greater than that of Al-PILC, 0.4369 h^{-1} , which indicates that adsorption of phosphate on LaAl-PILC occurred much faster than on Al-PILC.

3.4. Thermodynamic analysis

Temperature dependence of phosphate adsorption on the LaAl-PILC and Al-PILC has been investigated, and the adsorption isotherms are shown in Fig. 2. As shown in Fig. 2, the adsorption capacities of phosphate on both PILCs decrease with increasing temperature. This suggests that the interaction of phosphate and PILCs is exothermic in nature. The temperature dependence of adsorption process is associated with changes in thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption and were calculated according to the computing method of Das et al. [45]. ΔG° was obtained using the following relationship [8]:

$$\Delta G^\circ = -RT \ln b \quad (8)$$

where R is the gas constant, b the equilibrium constant obtained from Langmuir equation and T is the temperature (K). ΔH° and ΔS° were evaluated using Van't Hoff equation [8]:

$$\ln b \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Values of ΔH° and ΔS° were calculated by regression method from the slope and intercept of the Van't Hoff linear plot of $\ln b$ versus $1/T$. The thermodynamic parameters for phosphate adsorption on LaAl-PILC and Al-PILC are presented in Table 4. The negative

Table 4
Thermodynamic parameters for phosphate adsorption on LaAl-PILC and Al-PILC.

Sample	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
LaAl-PILC	25	-18.14	-61.33	-166.08
	30	-17.22		
	35	-16.48		
Al-PILC	25	-19.24	-36.73	-56.51
	30	-18.94		
	35	-18.67		

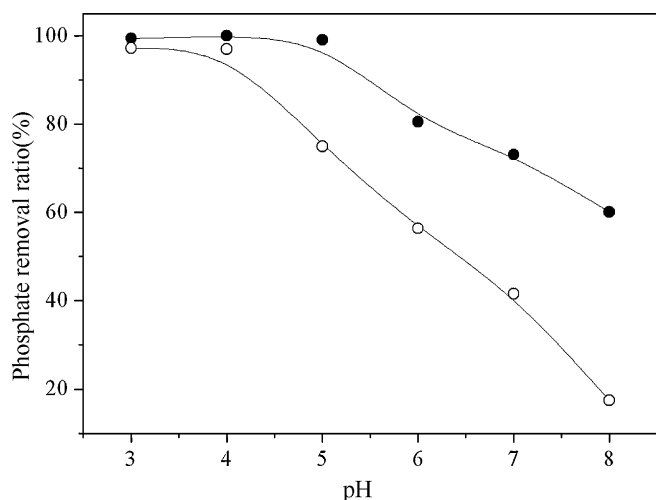


Fig. 4. Phosphate adsorption on LaAl-PILC (●) and Al-PILC (○) as a function of initial pH variation.

values of ΔG° at different temperatures indicate the spontaneous nature of phosphate adsorption. The negative value of ΔH° confirms the exothermic nature of adsorption. The positive values of ΔS° indicated a decreased randomness during the adsorption of phosphate onto PILCs.

3.5. Influence of initial pH on adsorption of phosphate

Initial pH of the aqueous solution is usually considered as an important variable that influences the adsorption of anions at water-adsorbent interfaces. The adsorption of phosphate on LaAl-PILC and Al-PILC were studied at various pH values ranging from 3.0 to 8.0 under the experimental conditions: initial phosphate concentration of 6.54 mgP/L, adsorbent dosage of 2.5 g/L and temperature of 25 °C. The results were shown in Fig. 4. The phosphate adsorption onto PILCs strongly depended on pH, the phosphate adsorption capacities of PILCs were improved significantly under the acid condition. It can be observed that the general shape of the pH curve has a turning point in adsorption for LaAl-PILC at pH 5 and for Al-PILC at pH 4, respectively. While at pH <5.0 for La/Al-PILC and at pH <4.0 for Al-PILC, the phosphate removal ratios retain maximum values, about 100% for La/Al-PILC and 97% for Al-PILC. With further increase in pH up to 8.0, there has been a steady decrease in the phosphate removal ratios for both PILCs. A similar trend was also observed for phosphate adsorption on Al clusters-pillared smectites, in which the phosphate adsorption amounts on Al clusters-pillared smectites increased sharply at around pH 6 toward lower pH and were at maximum in the pH range of 3.0–4.2 [19]. However, adsorption of phosphate by PILCs as a function of pH clearly differs from the pH response for montmorillonite. It has been observed that increasing phosphate adsorption on montmorillonite with increasing pH. This increased phosphate adsorption with increasing pH can be explained by the fact that montmorillonite contains a large amount of exchangeable calcium that can react with phosphorus to form an insoluble calcium phosphate phase such as apatite [16].

A higher pH causes the adsorbents surface to carry more negative charges and thus would more significantly repulse the negatively charged species in solution. Moreover, in the higher pH range, the concentration of hydroxide groups is too high, competing strongly with phosphate for the active sites. Therefore, the lower adsorption of phosphate at higher pH values resulted from an increased repulsion between the more negatively charged phosphate species and negatively charged surface sites and the

Table 5

Effects of concomitant anions on phosphate adsorption on LaAl-PILC and Al-PILC.

Anions added	Phosphate removal ratio (%)	
	LaAl-PILC	Al-PILC
PO ₄ ³⁻ (6.54 mg/L)	96.45	92.20
PO ₄ ³⁻ (6.54 mg/L) + NO ₃ ⁻ (0.5 mmol/L)	92.20	89.36
PO ₄ ³⁻ (6.54 mg/L) + SO ₄ ²⁻ (0.5 mmol/L)	92.20	78.01
PO ₄ ³⁻ (6.54 mg/L) + Cl ⁻ (0.5 mmol/L)	85.11	79.43
PO ₄ ³⁻ (6.54 mg/L) + HCO ₃ ⁻ (0.5 mmol/L)	70.92	69.50

competition between OH⁻ groups and phosphate species for the adsorption sites. In the pH range of 3–7, the predominant phosphate species is H₂PO₄⁻, which have a higher affinity for the La(III) center [7]. Thus, another reason of the high-phosphate sorption efficiency at lower pH is likely due to the nature of the phosphate species.

3.6. Influence of concomitant anions on adsorption of phosphate

Anions such as HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻ are mostly found in natural freshwater. As the concomitant anions are expected to interfere with the phosphate adsorption process by competing for the adsorption sites, the adsorption experiments were performed in the presence of various concomitant anions such as HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻, the results are illustrated in Table 5. It appears that both LaAl-PILC and Al-PILC adsorbed less phosphate in the presence of the four anions than for the case in which no anions were added. The effects of various concomitant anions on phosphate adsorption on the two PILCs are obviously different. The effects on adsorption of LaAl-PILC follow the order: HCO₃⁻ > Cl⁻ > SO₄²⁻ ≈ NO₃⁻. The order for Al-PILC is: HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻. The similar results have been reported by previous researchers on the adsorption of phosphate on the other solid adsorbents, such as for calcined layered double hydroxides (LDHs) [45]: SeO₃²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻, for lanthanum hydrate [31]: CO₃²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻. Among the four anions, HCO₃⁻ has strongest effect on the adsorption of phosphate on both LaAl-PILC and Al-PILC. The presence of 0.5 mmol/L HCO₃⁻ can reduce the phosphate removal ratio of LaAl-PILC s from 96.45% to 70.92%, and that of Al-PILC from 92.20% to 69.50%. In the presence of every anion, the reduction of phosphate removal ratio by Al-PILC is larger than that by LaAl-PILC, so the concomitant anions have more profound interfering effect on Al-PILC than that on LaAl-PILC.

Ion exchange reaction has been frequently proposed as a mechanism for phosphate adsorption, in which exchange occurs between phosphate ions and the hydroxide ions located at positively charged sites on the clay surface [16]. For both PILCs, the decreases in the adsorption capacity may be explained on the basis of ion exchange mechanism. It has been suggested that exchange can also take place by the binding of orthophosphate ions via displacement of lattice OH. If ion exchange played a significant role in the adsorption process, then the introduction of competing anions would have reduced the amount of phosphate adsorbed. Moreover, the orders of the effect of various anions on the phosphate adsorption may be related with affinity of adsorbents toward anions.

3.7. Stability of lanthanum

During the adsorption process, small amounts of lanthanum would be released from the LaAl-PILC to aqueous phase. In order to minimize the risk of metal leakage during adsorption of phosphate, the lanthanum stability is one of important aspects for LaAl-PILC as a phosphate adsorbent. The releasing behavior of

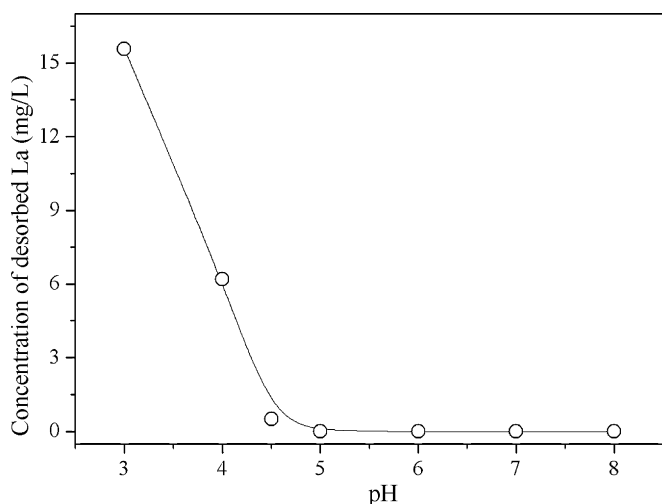


Fig. 5. The concentration of released lanthanum in water at various pH.

lanthanum from LaAl-PILC was investigated in solutions of different pH under the same conditions as the adsorption process of phosphate-containing water. The results are presented in Fig. 5. As shown in Fig. 5, the concentrations of residual lanthanum are intensively dependent on the pH of solution, the released amounts decrease gradually with the increase in pH. The pH dependency of lanthanum stability of LaAl-PILC is similar to that of the lanthanum-modified montmorillonite, reported by Yuan et al. [32]. However, the lanthanum in LaAl-PILC is more stable than that in lanthanum-modified montmorillonite in the whole pH range. Within the pH >5.0, the residual lanthanum concentrations of LaAl-PILC are near zero, lower than those of lanthanum-modified adsorbents such as lanthanum-modified montmorillonite [31] and lanthanum-doped mesoporous SiO₂ [30]. No lanthanum can be determined at higher pH regions, and the releasing amounts of lanthanum decrease gradually at around pH 4.5. Within the pH range of 3.0–8.0, the maximum concentration of residual lanthanum was less than 16 mgP/L. As mentioned above, the optimum pH for the adsorption of phosphate on LaAl-PILC is around 5.0 and the pH of natural freshwater is generally higher than 4.5, so the risk of lanthanum leakage during adsorption process is receivable. This result also implies that most of lanthanum ions were firmly bounded in the pillars of LaAl-PILC. Whereas the concentration of residual lanthanum ions decreased with increase of pH of the solution, which indicated more La(III) would be exchanged by H⁺ at acid conditions. And it is the bounded lanthanum ions that react with PO₄³⁻ and result in the removal of phosphate. Furthermore, with the increasing of pH, the release of lanthanum decreases and desorption of phosphate increase, the LaAl-PILC can therefore be effectively regenerated by base.

3.8. Recycling use of LaAl-PILC

From the cost and environmental point of view, a practical method of recycling the saturated adsorbent is necessary. As indicated by Figs. 4 and 5, while pH >5.0, with the increasing of pH, the release of lanthanum fixed on LaAl-PILC is nearly neglectable but the desorption of phosphate increase evidently. LaAl-PILC may therefore be effectively regenerated with strong base. The regenerability of LaAl-PILC can be revealed by the variation of Q_e/Q_{e0} (Q_e and Q_{e0} represent adsorption capacity of regenerated and fresh LaAl-PILC, respectively) with the used cycle (Fig. 6). In the six regeneration experiments, adsorption capacity of regenerated LaAl-PILC decreases gradually with the used cycle, but adsorption capacity of regenerated LaAl-PILC was always higher than 91% of that of the

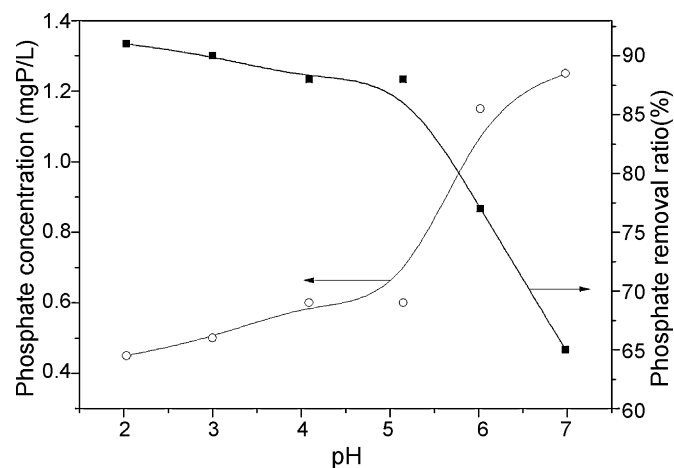


Fig. 6. Adsorption of phosphate on LaAl-PILC from phosphorus industry wastewater as a function of initial pH variation.

fresh LaAl-PILC (Fig. 6), which meant that the LaAl-PILC possessed a good regenerability.

3.9. Removal of phosphate from yellow phosphorus industry wastewater

In order to test the validity of LaAl-PILC for treating real effluents of water containing phosphate, LaAl-PILC was tested as an adsorbent for the removal of phosphate from wastewater produced in process of yellow phosphorus. The variations of phosphate removal efficiency with pH are shown in Fig. 7. As shown in Fig. 6, phosphate in wastewater can be reduced from 5 to 0.45–1.25 mgP/L under conditions of various initial pH. Analogous to the results mentioned in Section 3.5, the phosphate adsorption onto PILCs strongly depends on initial pH. The phosphate removal efficiency varies between 65% and 91% with the pH range of 2–6, decreases obviously while pH >5.0. As shown in Fig. 4, under similar conditions with a synthetic phosphate solution containing 5 mgP/L (without added anions), the phosphate removal efficiency decreased from about 100% to 60% with the increase of pH from 3 to 8. The reduction in phosphate adsorption from real industry wastewater might be ascribed to the competitive effect of concomitant anions.

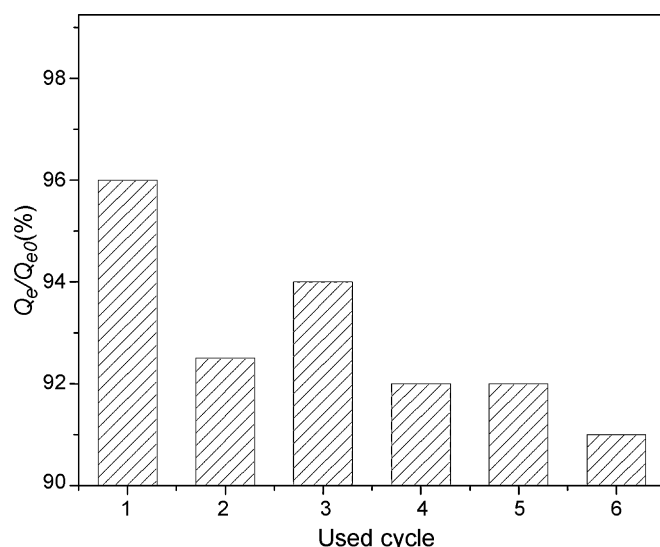


Fig. 7. Variation of adsorption capacity influenced by LaAl-PILC used cycle.

4. Conclusion

In this study, it was observed that LaAl-PILC and Al-PILC exhibit interesting variations in their adsorption properties with regard to removal of phosphate from water. LaAl-PILC was proved to be much more efficient adsorbent than Al-PILC for the removal of phosphate from water. Both Langmuir and Freundlich equations were fitted to adsorption isotherms of LaAl-PILC and Al-PILC satisfactorily. Adsorption kinetics of both PILCs obeyed a pseudo-first-order kinetic model. The thermodynamic parameters revealed that the process was exothermic and spontaneous. The phosphate adsorption capacities of PILCs were improved significantly under the acid condition. Competing anions in solution had strong effect on phosphate adsorption on LaAl-PILC. Lanthanum loaded on LaAl-PILC is stable enough to be used at pH >4.5. The validity of LaAl-PILC for treating real effluents of water containing phosphate and regenerability were also tested.

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