Study on an effective industrial waste-based adsorbent for the adsorptive removal of phosphorus from wastewater: equilibrium and kinetics studies
Ruzhen Xie, Yao Chen, Ting Cheng, Yuguo Lai, Wenju Jiang and Zhishan Yang

ABSTRACT
In this work, an effective adsorbent for removing phosphate from aqueous solution was developed from modifying industrial waste — lithium silica fume (LSF). The characterization of LSF before and after modification was investigated using an N2 adsorption–desorption technique (Brunauer–Emmett–Teller, BET), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Studies were conducted to investigate the effect of adsorbent dose, initial solution pH, contact time, phosphate concentration, and temperature on phosphate removal using this novel adsorbent. The specific surface area for modified LSF (LLSF) is 24.4024 m²/g, improved 69.8% compared with unmodified LSF. XRD result suggests that the lanthanum phosphate complex was formed on the surface of LLSF. The maximum phosphate adsorption capacity was 24.096 mg P/g for LLSF, and phosphate removal was favored in the pH range of 3–8. The kinetic data fitted pseudo-second-order kinetic equation, intra-particle diffusion was not the only rate controlling step. The adsorption isotherm results illustrated that the Langmuir model provided the best fit for the equilibrium data. The change in free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) revealed that the adsorption of phosphate on LLSF was spontaneous and endothermic. It was concluded that by modifying with lanthanum, LSF can be turned to be a highly efficient adsorbent in phosphate removal.

Key words | adsorption, kinetics, lithium silica fume, phosphate

INTRODUCTION
Phosphorus is an unrenewable resource which is essential for the growth of organisms in ecosystems. However, excess of bioavailable phosphorus lead to eutrophication in water bodies, resulting the bloom of aquatic plant and algal growth, and cause dissolved oxygen depletion.

Phosphates (P) may come from agricultural fertilizers and other sources such as treated and untreated sewage, which is present in organic matter and also in soaps and detergents (Kuroki et al. 2014). It is of great importance to remove phosphates from wastewater before being dispersed into environment (Xie et al. 2014a). Typical removal methods such as biological treatment (Lopez-Vazquez et al. 2008), chemical precipitation (Lu & Liu 2010), ion exchange (Chubar et al. 2005), membrane filtration (Kim et al. 2008) and adsorption (Kuroki et al. 2014) have been successfully applied. Among them, biological P removal is limited in low concentration, chemical precipitation has been hindered by its high chemical consumption and excessive production of chemical sludge (Fang et al. 2014). Ion exchange may lose its uptake capability after multiple regenerations, while membrane filtration is limited by fouling and it is economically unattractive (Awual & Jyo 2011). Adsorption is recommended as one of the most effective immobilization processes for treating P. Adsorptive removal of P is high efficiency and easy handling even at low P concentration. Various adsorbents such as bentonite (Kuroki et al. 2014), zeolite (Jiang et al. 2015), red mud (Zhao et al. 2011), lanthanum hydroxide (Xie et al. 2014b) and iron-related adsorbents (Chen et al. 2015) were successfully used in the adsorptive removal of phosphate. However, the high cost of these adsorbents is the main obstacle for their wide application.

Lithium silica fume (LSF) is a byproduct of silicon or alloys containing silicon industry. The main constituents of LSF are SiO₂ and Al₂O₃ (Siddique 2011), containing some

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trace element such as iron, magnesium, calcium, and alkali oxides. Silicon fume has remarkable physical and chemical properties such as high chemical stability, extremely small particle size, large surface area, and high electrical resistivity (Siddique 2021), which make it a potentially attractive adsorbent.

Lanthanum compounds are highly active in P adsorption, phosphate precipitation by lanthanum with molar ration of 1:1 formed lanthanum–phosphate complex, which is known to be the least soluble among the rare earth-phosphate salts and able to form when present in low concentrations and at low pH values = 4 (Diatloff et al. 1993; Haghseresht et al. 2009). Many researchers trying to develop efficient P adsorbent by doping lanthanum to various kinds of material, such as bentonite (Spears et al. 2013), zeolite (Xie et al. 2014a) and montmorillonite (Tian et al. 2009), red mud (Zhao et al. 2011), et al. The resulting adsorbents showed remarkable improvement in P removal after doping with lanthanum; however, these materials are not easily accessible and are not cheap.

The emphasis of this work is to study the feasibility of using LSF, an industrial waste, for the removal of phosphorus from aqueous solution. The surface structure of the materials was investigated by means of scanning electron microscope, an N₂ adsorption–desorption technique (Brunauer–Emmett–Teller, BET), and X-ray diffraction (XRD). The effects of temperature and pH on phosphate adsorption capability were investigated. Moreover, the phosphate adsorption equilibrium, kinetics and thermodynamics by these novel adsorbents were described for further understanding of the adsorption mechanism.

**MATERIALS AND METHODS**

**Materials and characterizations**

The LSF used in the present study was obtained from a Regenerated Resources Recycling Co., Ltd of Sichuan Province, China. The chemical compositions of the LSF consists primarily of SiO₂ (60 wt.%), Al₂O₃ (18.33 wt.%), SO₃ (6.08 wt.%), and CaO (4.28 wt.%). There are also small amounts of alkali metals (K₂O 0.73%, Li₂O 0.43%, Na₂O 0.56%), iron metal oxides (Fe₂O₃ 0.56%), etc. All the chemicals including LaCl₃·7H₂O, KH₂PO₄, NaOH, HCl and H₂SO₄ were of analytical grade, which were obtained from Kelong Chemical Co. (China) and used as received.

Raw LSF with particle size <75 μm was selected for subsequent modification. After dried in oven at temperature of 110 °C to constant weight, 10 g of LSF was dispersed into 50 mL 0.08 mol/L LaCl₃·7H₂O solution, the pH was adjusted to 11.0 by dropwise adding 1 M NaOH under vigorous stirring. Afterwards, the solution was kept for 24 h before separating the solids and liquid. The resulting solids were washed with deionized water until pH neutral and dried at 110 °C, and then cooled in a desiccator. The modified LSF with lanthanum (III) solution was symbol as LLSF.

The crystallinity and phase identification of LSFs were determined by XRD (X-Pert PRO MPD) with Cu Ka as the radiation source under 36KV with 20 range of 10–80. The scanning electron microscopy (SEM) measurement was carried out using SEM (JSM7500F from JEOL Company). The specific surface areas and pore volumes were analyzed by using the N₂ adsorption–desorption method (Micromeritics ASAP 2460). The amount of lanthanum determination is analysis by X-ray fluorescence spectrometry (XRF-1800, Japan). pH point of zero charge (pHZC) was measured to investigate the total surface charge of the adsorbents using the method described by Moharami and Jalali (Moharami & Jalali 2013).

**Equilibrium adsorption and desorption**

A series of batch tests were conducted to investigate the phosphate adsorption performances of LSFs. Phosphate solution was prepared by dissolving anhydrous K₂HPO₄ in deionized water. Typically, different dosage of the as-prepared adsorbent was added into 100 mL of 1.50 mg P/L phosphate solution in sealed conical flasks. After being shaken for a certain time at room temperature (25 ± 1 °C) at 120 rpm, the suspensions were filtered and the concentration of phosphate was analyzed according to ammonium molybdate spectrometric method by UV–visible spectrophotometer (Jiang et al. 2013). The effect of pH on phosphate removal was obtained by adding 0.1 M NaOH or 0.1 M HCl solution to desired pH values ranging from 1 to 10 with 100 mL solution containing 1 mg/L phosphate. Adsorption kinetic studies were carried out as follows: 1.6 g of LSFs was added in 800 mL phosphate solution with different initial concentrations of 1 mg/L, 10 mg/L, and 50 mg/L, respectively. The suspension was continuous mixing by magnetic stirrers for 8 h at room temperature (25 ± 1 °C) with an initial solution pH of 7. Samples were taken at various times during the adsorption process. An adsorption isotherm study was carried out by shaking 0.2 g of LSFs in 100 mL KH₂PO₄ solutions with different initial concentrations (5, 10, 15, 25, 30, 50, 100, 200 mg/L) for 24 h at room temperature (25 ± 1 °C) and the absorbance was measured at 822 nm.

**Adsorption isotherm**

A series of batch tests were conducted to investigate the adsorption isotherms using different LSF concentrations in 100 mL of various phosphate solution concentrations at room temperature. The LSF was added to the solution and allowed to equilibrate for 24 h before filtering and analyzing the adsorption capacity of the materials. The resulting phosphate concentration was measured using an UV–visible spectrophotometer (Jiang et al. 2013). The equilibrium data were fitted to the Langmuir (Eq. 1), Freundlich (Eq. 2), and Redlich–Peterson (Eq. 3) isotherms to determine the adsorption capacity and equilibrium constants.

**Langmuir isotherm**

\[
Q_e = \frac{Q_m b C_e}{1 + b C_e}
\]

where \(Q_e\) is the amount of phosphate adsorbed at equilibrium (mg/g), \(Q_m\) is the maximum adsorption capacity (mg/g), \(b\) is the Langmuir constant related to free energy of adsorption (L/mg), and \(C_e\) is the equilibrium concentration of phosphate (mg/L).

**Freundlich isotherm**

\[
Q_e = K_F C_e^1/n
\]

where \(K_F\) is the Freundlich constant related to adsorption capacity (mg/g L\(^{1/n}\)) and \(n\) is the Freundlich exponent which indicates the adsorption intensity.

**Redlich–Peterson isotherm**

\[
Q_e = \frac{Q_m b C_e}{1 + b C_e + b C_e^2}
\]

where \(b\) is the Redlich–Peterson constant related to the free energy of adsorption (L/g).

**Adsorption kinetics**

A series of batch tests were conducted to investigate the adsorption kinetics using different LSF concentrations in 100 mL of various phosphate solution concentrations at room temperature. The LSF was added to the solution and allowed to equilibrate for 24 h before filtering and analyzing the adsorption capacity of the materials. The resulting phosphate concentration was measured using an UV–visible spectrophotometer (Jiang et al. 2013). The equilibrium data were fitted to the pseudo-first-order (Eq. 4), pseudo-second-order (Eq. 5), and Elovich (Eq. 6) kinetic models to determine the adsorption rate and equilibrium time.

**Pseudo–first–order**

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where \(q_t\) is the amount of phosphate adsorbed at time \(t\) (mg/g) and \(k_1\) is the pseudo–first–order rate constant (mg/g min\(^{-1}\)).

**Pseudo–second–order**

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(k_2\) is the pseudosecond-order rate constant (g/mg min).
50, 75, and 100 mg/L) for 6 h under 25, 30, 35 and 45 °C, with initial solution pH of 7.

Desorption experiments conducted to explore the recovery of the phosphate were carried out with pre-sorbed P-saturated LLSF. For the desorption tests, the phosphate-containing LLSF were added into 100 mL 0.1–4.5 M NaOH solution. The mixture was stirred for 6 h and then separated from the NaOH solution.

All the above procedures were repeated and the average values were used for analysis. The removal rate (%) and adsorption capacity ($q_e$) of phosphate were calculated by the following equations:

Removal rate (%) = \( \frac{C_0 - C_e}{C_0} \times 100 \)  

\[ q_e = \frac{(C_0 - C_e)V}{M} \]

### Adsorption isotherms

Adsorption isotherms data were fitted using Langmuir, Freundlich and Temkin isotherm equations, as shown in Equations (3)–(5), respectively (Xie et al. 2013):

\[ \frac{C_e}{q_e} = \frac{1}{Q_mK_L} + \frac{1}{Q_m} \]  

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

\[ q_e = B_T \ln A_T + B_T \ln (C_e) \]  

in which $Q_m$ is the theoretical maximum monolayer adsorption capacity when the LLSF surface is completely covered with phosphate (mg/g), $C_e$ is the equilibrium concentration of phosphate in the solution (mg/L), $q_e$ is the amount of phosphate adsorbed at specified equilibrium (mg/g), $B_T$ is Temkin constant, $K_L$ (L/mg), $K_F$ ((mg/g) (L/mg) 1/n) and $A_T$(L/min) are binding constants for Langmuir, Freundlich and Temkin models, respectively. $n$ is Freundlich exponent related to the adsorption intensity (Li et al. 2013).

### Adsorption thermodynamics

The thermodynamic parameters of phosphate adsorption on LLSF can be evaluated according to the following equations:

\[ \Delta G^0 = -RT \ln k_d \]  

\[ \ln k_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

in which $R$ (8.314 J/(mol K)) is the gas constant, $T$ (K) is the absolute temperature, $K_d$ is the thermodynamic equilibrium constant of the adsorption process (Chen et al. 2011). $\Delta H^0$ and $\Delta S^0$ values were evaluated according to Van’t Hoff equation.

### Adsorption kinetic study

Both pseudo-first-order and pseudo-second-order mechanisms were applied to study the LLSF adsorption mechanism. They are represented in the following forms (Xie et al. 2013):

\[ \log \left( \frac{q_e - q_t}{q_t} \right) = \log \frac{q_e}{k_1} - \frac{k_1}{2.303}t \]  

\[ t = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \]

in which $q_t$ and $q_e$ are the amounts of P adsorbed (mg/g) at equilibrium and time t (h), respectively. $k_1$ and $k_2$ (g/mg h) are rate constants of pseudo-first-order adsorption (1/h), and second-order adsorption (g/mg h).

In order to identify the role of diffusion in P adsorption on LLSF, the intra-particle diffusion rate affecting adsorption was studied using the intra-particle diffusion model as following (Benyoucef & Amrani 2011):

\[ q_t = k_{id}t^{1/2} + C \]  

in which $k_{id}$ is the constant of intra-particle diffusion rate (mg/(g h^{1/2})) and $C$ is proportional to the extent of the boundary layer thickness.

### RESULT AND DISCUSSION

#### Characterization of adsorbents

SEM was employed to determine the surface of LSFs before and after modification with lanthanum (III). The
micrograph shows that both LSF and LLSF have porous structures, their surface morphology are slightly different. Rougher surface and larger porosity can be observed from LLSF as shown in Figure 1(b), this could be due to flocs of lanthanum hydroxide that appeared on LSF surface, which is supported by XRD results.

Table 1 shows the specific surface areas and total pore volumes of the LSF and LLSF. The N$_2$ adsorption/desorption isotherm showed a mesoporous pattern. As can be seen from Table 1, the raw LSF has a surface area of 14.3683 m$^2$/g with an average diameter of 9.02 nm. After lanthanum (III) modification, the surface area of LLSF increased 69.8% and reached 20.4024 m$^2$/g, the average diameter increased to 11.3 nm. An increment of total pore volume was also observed, while micropore volume decreased 3.2%, suggesting some amount of mesopores or macropore were formed on LSF surface after lanthanum (III) modification.

The XRD pattern of LSFs before and after lanthanum (III) treatment was shown in Figure 2(a) and 2(b), reflection of La was observed in LLSF. Figure 2(c) illustrates LLSF after reacting 6 h and reach saturation in 1 mg P/L solution. The peak intensity of quartz (26.19°, 20) in three XRD patterns indicated SiO$_2$ was the main mineral component in LSFs. The diffraction pattern for LLSF saturated with phosphate (Figure 2(c)) suggests that the lanthanum phosphate complex was formed on the surface of LLSF. This newly-emerged peaks refers to a monoclinic LaPO$_4$ phase, with cell parameters of $a = 0.6837$ nm, $b = 0.7077$ nm, $c = 0.6510$ nm, $\alpha = c = 90^\circ$, $b = 103.25^\circ$ (JCPDS Card No. 32-0493) (Xie et al. 2014a). The XRF results show no La element was found in the raw LSF, and after lanthanum (III) treatment, 5.39 wt.% La$_2$O$_3$ existed on LLSF, which confirms the presence of La on XRD analysis.

**Effect of LSF dose**

The effect of LSF dosage on P removal was shown in Figure 3. It can be observed that P removal rate increases with LSF dose increase. By increasing dosage, more adsorption sites are available for a certain amount of P, and the diffusion of P onto LLSF surface became easier, thus higher removal rate was achieved with increasing LLSF dosage. As can be seen from Figure 3, LLSF exhibits higher adsorption capacity towards P than LSF, 95.44% removal rate was observed with an LLSF dose of 0.3 g.
(100 mL), compared with 11.03% achieved by LSF with the same dosage. Further increment of dosage does not significantly change the P removal rate.

**Effect of pH**

The aqueous solution pH is an important factor that influences the adsorption capacity on the solid–liquid interfaces. The effect of pH on phosphate adsorption onto LLSF was studied with pH value between 1 and 10 as shown in Figure 4. It can be found that the adsorption of phosphate on LLSF was strongly pH dependent, the phosphate adsorption increased with pH increases from 1 to 3, and kept steady in a pH range of 3–8. The zero point of charge (pH_{PZC}) of LLSF is 7.8; at pH values lower than 7.8, the surface of LLSF was protonated and showed as positively charged, which would favor the electrostatic attraction to phosphate species H$_2$PO$_4$$^-$, which is the main species in the solution between pH 3–8 (Huang et al. 2015). With a pH value higher than 8, large amounts of OH$^-$ would compete with H$_3$PO$_4$ and HPO$_4^{2-}$ for adsorption sites, the phosphate adsorption tends to decrease. From Figure 4, we can see the phosphate adsorption amount reduced from 1.23 mg/g to 0.92 mg/g when pH increased from 8 to 10. Similar trends were also observed for phosphate adsorption on bentonite (Haghseresht et al. 2009).

Thermodynamic calculations by MINEQL + showed that four species of phosphate exist in solution, which is H$_3$PO$_4$, H$_2$PO$_4$, HPO$_4^{2-}$ and PO$_4^{3-}$ with different ratios according to pH (Chubar et al. 2005). Phosphate acid undergoes dissociation and H$_2$PO$_4$ and HPO$_4^{2-}$ are superior in solution form with a solution pH between 8 and 10 (Ye et al. 2006). Moreover, in this pH range, the LLSF surfaces carry more negative charges and thus would significantly repulse the negatively charged species in solution (Ye et al. 2006). As a result, the P adsorption amounts decreased.

**Adsorption kinetics**

The adsorption kinetic study was carried out using LLSF with different initial P concentration solution of 1 mg/L,

![Figure 2](https://iwaponline.com/wst/article-pdf/73/8/1891/462379/wst073081891.pdf)

Figure 2 | XRD patterns of LSF (a), LLSF (b), and LLSF after adsorbing phosphate (c).
10 mg/L and 50 mg/L, respectively. As shown in Figure 5, the adsorption of phosphate was strongly dependent on its initial P concentration. The adsorption capacity of LLSF achieved 0.499 mg P/g within 6 h in 1 mg/L P solution, 6 h of 4.493 mg P/g in 10 mg/L P solution, and 7 h of 17.598 mg P/g in 50 mg/L P solution. It is obvious that a longer time was needed to reach equilibrium in higher P concentration solution, and also a larger adsorption amount was achieved in higher P concentration solution. It should also be noted that, unmodified LSF only achieved phosphate adsorption capacity of 0.37 mg P/g, 0.85 mg P/g, and 0.88 mg P/g for initial concentration of 1 mg/L, 10 mg/L and 50 mg/L, respectively. It is strongly proved that the lanthanum (III) modification greatly enhances the phosphate adsorption on LSFs.

In order to further study the kinetic mechanism that controls the phosphate adsorption, pseudo-first-order model and pseudo-second-order model (Figure 5(a)) were employed to fit the experimental data. The corresponding parameters are listed in Table 2. From Table 2, we could see pseudo-second-order was better fitted than pseudo-first-order model, which suggests chemisorption might be involved in the adsorption process. Similar results were found in lanthanum-loaded tourmaline (Li et al. 2015), betonies (Kuroki et al. 2014) and oak sawdust (Wang et al. 2015). The initial adsorption rate (h) derived from the adsorption kinetic data using different initial P concentration of 1 mg/L, 10 mg/L and 50 mg/L are 40.323 mg/(g.h), 121.951 mg/(g.h) and 178.571 mg/(g.h), respectively. It confirms that faster removal rate was achieved under higher P concentration.

To further understanding the diffusion mechanism, we studied intra-particle diffusion model in the adsorption process. As can be seen in Figure 5(b), the linear fit of intra-particle diffusion model presents three linear portions, which indicates multi-stage adsorption process was involved. The first sharper portion is caused by the external surface adsorption or instantaneous adsorption which is driven by the initial phosphate concentration differences (Huang et al. 2014). The second linear portion is the gradual adsorption stage where the intra-particle diffusion is the
rate-limiting step. The third portion is attributable to the final equilibrium state in which the intra-particle diffusion slows down due to less residual phosphate remains in the solution. As can be seen from Table 2, kid1, kid2 and kid3 increase with increasing initial phosphate concentration, which could be attributed to higher concentration, provides a higher gradient which drives P into the pores. At the same initial concentration, the value of kid2 is greater than kid3, suggesting that intra-particle diffusion controls the process of adsorption (Xu et al. 2013).

Adsorption isotherms

To further investigate the P adsorption capacity, Langmuir, Freundlich and Temkin adsorption isotherms were studied with various initial phosphate concentration at 25, 30, 35 and 45°C. The theoretical parameters of adsorption isotherms along with regression coefficients are reported in Table 3. The calculated adsorption isotherms compared with the experimental data are presented in Figure 6. From Table 3 and Figure 6, we can see all the isotherm exhibited a rapid rise in the adsorption capacity with increasing equilibrium concentration, and Langmuir model fits best with the equilibrium data. The applicability of adsorption models for the three isotherms approximately followed the order: Langmuir > Temkin > Freundlich, which suggests the homogeneous nature of the LLSF. The maximum adsorption capacity for monolayer saturation increased with temperature increasing, and achieved 24.096 mg P/g at 45°C, which shows an endothermic process. Freundlich constant 1/n was smaller than 1, indicating LSF adsorbing P is a favorable process (Wang et al. 2010).

Adsorption experiments were conducted at 25, 30, 35 and 45°C to investigate the effect of temperature, with initial P concentration of 5–100 mg/L, LLSF dosage of 2 g/L, pH = 7. Positive value of △Hº of 25.007 KJ/mol can be observed from Table 4, which indicates that the adsorption process is endothermic, and a chemical reaction such as ion-exchange is involved during the adsorption process (Silva et al. 2013). The negative values of △Sº at 25–45°C indicates that the adsorption of phosphate onto LLSF is spontaneous. The values of △Sº were positive, thus indicating a good affinity of phosphate ions towards LLSF. The increases in adsorption capacity of phosphate at higher temperatures may be caused by the enlargement of pore size and/or activation of the LLSF surface (Benyoucef & Amrani 2014).

Table 2 | The pseudo-first-order, pseudo-second-order and intra-particle diffusion model constants and correlation coefficient for LLSF adsorbing different concentration P solution (1, 10, and 50 mg/L)

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>qe, exp (mg/g)</th>
<th>qe, cal (mg/g)</th>
<th>k1</th>
<th>R²</th>
<th>qe, cal (mg/g)</th>
<th>k2</th>
<th>h</th>
<th>mg/(g·h)</th>
<th>R²</th>
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<tr>
<td>1</td>
<td>0.499</td>
<td>0.0222</td>
<td>1.119</td>
<td>0.9112</td>
<td>0.500</td>
<td>161.129</td>
<td>40.323</td>
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<td>10</td>
<td>4.493</td>
<td>0.428</td>
<td>0.747</td>
<td>0.8744</td>
<td>4.517</td>
<td>5.978</td>
<td>121.951</td>
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<td>50</td>
<td>17.598</td>
<td>2.888</td>
<td>0.434</td>
<td>0.9721</td>
<td>17.730</td>
<td>0.568</td>
<td>178.571</td>
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Intra-particle diffusion model

<table>
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<tr>
<th>Initial concentration (mg/L)</th>
<th>kid1 mg/(g·h^(1/2))</th>
<th>C1</th>
<th>R²</th>
<th>kid2 mg/(g·h^(1/2))</th>
<th>C2</th>
<th>R²</th>
<th>kid3 mg/(g·h^(1/2))</th>
<th>C3</th>
<th>R²</th>
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<tr>
<td>1</td>
<td>1.129</td>
<td>0</td>
<td>1</td>
<td>0.042</td>
<td>0.455</td>
<td>0.9337</td>
<td>0.002</td>
<td>0.495</td>
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<tr>
<td>10</td>
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<td>0</td>
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<td>1.059</td>
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<td>50</td>
<td>34.354</td>
<td>0</td>
<td>1</td>
<td>2.851</td>
<td>13.207</td>
<td>0.9492</td>
<td>0.763</td>
<td>15.511</td>
<td>0.9821</td>
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Table 3 | Langmuir, Freundlich, and Temkin adsorption isotherm parameters for LLSF adsorbing P at 25°C, 30°C, 35°C and 45°C, respectively

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T (°C)</th>
<th>Qm (mg/g)</th>
<th>K (L/mg)</th>
<th>R²</th>
<th>Qm (mg/g)</th>
<th>K (L/mg)</th>
<th>1/n</th>
<th>R²</th>
<th>A0 (mmol/g)</th>
<th>B0</th>
<th>R²</th>
</tr>
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<tbody>
<tr>
<td>LLSF</td>
<td>25</td>
<td>23.866</td>
<td>0.174</td>
<td>0.9986</td>
<td>3.967</td>
<td>0.474</td>
<td>0.9566</td>
<td>2.689</td>
<td>4.454</td>
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<tr>
<td></td>
<td>30</td>
<td>23.889</td>
<td>0.217</td>
<td>0.9976</td>
<td>4.490</td>
<td>0.451</td>
<td>0.9464</td>
<td>3.225</td>
<td>4.363</td>
<td>0.9783</td>
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</tr>
<tr>
<td></td>
<td>35</td>
<td>24.096</td>
<td>0.293</td>
<td>0.9961</td>
<td>5.315</td>
<td>0.421</td>
<td>0.9392</td>
<td>4.947</td>
<td>4.191</td>
<td>0.9587</td>
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<td></td>
<td>45</td>
<td>24.096</td>
<td>0.461</td>
<td>0.9947</td>
<td>6.857</td>
<td>0.354</td>
<td>0.957</td>
<td>13.022</td>
<td>3.592</td>
<td>0.9519</td>
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</table>
As can be seen from Table 5, lanthanum hydroxide has the highest adsorption capacity towards phosphate; however, lanthanum hydroxide is a relatively expensive material for phosphorus removal. Granulated ferric hydroxide (GFH) can remove phosphate well, and GFH is less expensive; however, 96 h contact time is needed for GFH to reach equilibrium, and GFH is highly dissolvable in acidic solution (Genz et al. 2004). Our LLSF shows greater adsorption capacity than some other adsorbents.

Table 5 | Maximum P adsorption capacity on some adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Phoslock</td>
<td>9.5–10.5</td>
<td>Haghseresht et al. (2009)</td>
</tr>
<tr>
<td>Lanthanum(III) modified bentonite</td>
<td>14.0</td>
<td>Kuroki et al. (2014)</td>
</tr>
<tr>
<td>Granulated ferric hydroxide (GFH)</td>
<td>23.3</td>
<td>Genz et al. (2004)</td>
</tr>
<tr>
<td>Fe(III)-modified bentonite</td>
<td>11.15</td>
<td>Zamparas et al. (2012)</td>
</tr>
<tr>
<td>Commercial La(OH)3</td>
<td>55.56</td>
<td>Zamparas et al. (2013)</td>
</tr>
<tr>
<td>Modified palygorskites</td>
<td>8.31</td>
<td>Ye et al. (2006)</td>
</tr>
<tr>
<td>LLSF</td>
<td>24.10</td>
<td>This study</td>
</tr>
</tbody>
</table>

As can be seen from Table 5, lanthanum hydroxide has the highest adsorption capacity towards phosphate; however, lanthanum hydroxide is a relatively expensive material for phosphorus removal. Granulated ferric hydroxide (GFH) can remove phosphate well, and GFH is less expensive; however, 96 h contact time is needed for GFH to reach equilibrium, and GFH is highly dissolvable in acidic solution (Genz et al. 2004). Our LLSF shows greater adsorption capacity than some other adsorbents.
Desorption

High stability and reusability are important features for an advanced adsorbent. Desorption studies were carried out using P-adsorbed La(III)-loaded LSF at different NaOH concentration. It was found that the amount of the desorbed P increased with increasing NaOH concentration Figure 7. In 0.1 M NaOH, 1.96% of the phosphorus could be released into the solution. However, more phosphate was desorbed by increasing NaOH concentration, and about 90% phosphorus release was observed in 4M NaOH solution. Further increment of NaOH concentration to 4.5 M, does not show obvious increasing of phosphate release. The results indicate that P adsorption on the LLSF is a complicated process, electrostatic attraction, ion exchange and chemical precipitation processes might be involved in P adsorption on LLSF. The adsorption is not completely reversible in 0.1-4.5M NaOH solution. The phosphorus adsorbed by electrostatic attraction and ion exchange could be easily desorbed, while phosphorus removed by complex formation could not be desorbed.

CONCLUSION

This study shows LLSF is effective for the removal of phosphate from aqueous solution, Langmuir isotherm best fitted the equilibrium data, and the maximum adsorption capacity was 24.096 mg P/g. pH and desorption studies showed that both chemisorption and ion exchange are involved in the adsorption process.

Adsorption kinetic data were adequately fitted by the pseudo-second-order kinetic model and, although intra-particle diffusion was not the only rate controlling step, it still played a significant role in the adsorption mechanism. Thermodynamic studies demonstrate that the adsorption process was endothermic and spontaneous in nature.

REFERENCES


