Removal of phosphate from polluted water by lanthanum doped vesuvianite

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ABSTRACT

The adsorption capacities of vesuvianite and lanthanum doped vesuvianite were studied. The effects of different mass ratios of La/vesuvianite at different contact times, pHs, and temperatures on adsorption capacity were also studied. It was found that lanthanum doped vesuvianite exhibited higher adsorption capacity than undoped one due to the reaction of bounded lanthanum with phosphate. The adsorption capacity of lanthanum doped vesuvianite for phosphate removal increased with the increase of La/vesuvianite mass ratio. The Freundlich and Langmuir models were used to simulate the sorption equilibrium, and the results indicate that the Langmuir model had a better correlation with the experimental data than the Freundlich model did. When the initial phosphate concentration was 1 mg P/L, the adsorptive capacity rate would be 1.32 mg P/g lanthanum doped vesuvianite (La/vesuvianite mass ratio ≥ 0.14) at pH between 6 and 9 after 40 h. The concentrations of residual lanthanum ions in solution at different conditions were measured. Lanthanum doped vesuvianite was also used for the removal of phosphate in a polluted river water and it could be easily recycled once without losing its activity to a greater extent.

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1. Introduction

Phosphate (P) is usually considered to be the limiting nutrient with respect to the eutrophication of natural water bodies. Therefore, it is desirable that water treatment facilities remove phosphate from the wastewater before it is returned to the environment. Various techniques have been used for phosphate removal. Among these, chemical precipitation, adsorption and biological methods have been successfully applied. Adsorption is one of the techniques to remove phosphate, which is comparatively more useful and more efficient [1]. Most of hydrate can adsorb anions, such as PO_4^{3-} [2]. For example, aluminum and aluminum oxides [3–5], iron and iron oxides [6–8], fly ash [1,9], slag [10], calcite [11], and red mud [12] and Al/SBA-15 [13], La/mesoporous SiO_2 [14] were used to remove phosphate. Recently, modified coal fly ash [15], palygorskites [16] and coir pith [17] have been used for the removal of phosphate. However, same as all the methods mentioned above, they would be very difficult to be regenerated since these materials would be sunk down to the bottom of the water bodies.

In contrast, vesuvianite would be a good choice because of its low density (<800 kg/m^3) and pore morphologies [18], which make vesuvianite float on the surface of water. Vesuvianite is an ortho-disilicate mineral, with a very complex structure and an approximate formula of $Ca_{19}(Al, Fe)_{10}(Mg, Fe)_3[Si_2O_7]_4[SiO_4]_{10}(O, OH, F)_{10}$ [19] which is still under discussion [20]. Furthermore, good physical strength, high chemical stabilities, and environmental friendliness make vesuvianite is a very attractive support material [18]. Vesuvianite has also been locally used in building and landscaping due to its properties of acid–alkali-resistant, high hardness, lightweight, sound insulation, antiskid and strong resistibility of effloresce and high temperature [21]. On the other hand, lanthanum exhibited more adsorptive capability for phosphate compared with transitional metals [22], and suitable lanthanum may be nontoxic and environment-friendly [23]. Therefore, it was suggested a good possibility to apply lanthanum doped vesuvianite (La-Ves), for the first time for the removal of phosphate. However, so far, there is no report on using La-Ves to remove phosphate in polluted water that we can find.

2. Materials and methods

2.1. Vesuvianite modified by lanthanum

The vesuvianite used in our study was obtained from Tengchong, a town in northwestern part of Yunnan Province in China. The color of vesuvianite was grey-black. Feldspar and pyroxene were the essential mineral components of vesuvianite, and minor mineral components were olivine, quartz, zeolite and so on.

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A brief description of the procedure for syntheses of La-Ves is as follows: 0.3 g vesuvianite was introduced to solutions containing different amounts of lanthanum precursor [La(NO$_3$)$_3$·6H$_2$O] so that different La/Ves mass ratios (0.035, 0.07, 0.14 and 0.16) were prepared. After 40 h, the vesuvianite was taken out, dried at 90 °C for 3 h and calcined at 400 °C in air for 3 h. The samples were denoted as Lax-Ves where x indicated the La/Ves mass ratio. For comparison, undoped vesuvianite was also prepared.

2.2. Material characterizations

Major elements were determined by X-ray fluorescence spectrometry (XRF, ZSX 100 e) at 50 kV and 50 mA. X-ray diffraction (XRD) patterns of all grounded samples were obtained with a Rikaku diffractometer using Cu Kα radiation at 40 kV and 30 mA over the range of 5–80°. Fourier transform infrared (FT-IR) measurements were performed on a Thermo Nicolet FT-IR 8700 instrument. Potassium bromide pellets containing 0.5% of the catalyst were used in FT-IR experiments and 125 scans were accumulated for each spectrum in transmission, at a spectral resolution of 4 cm^{-1}. The spectrum of dry KBr was taken for background subtraction.

2.3. Measurements of adsorptive capacity

Phosphate removal for samples was acquired through batch experiments. Samples weighing 0.3 g were added into a beaker with 1 L of solution containing phosphate. The pH of solution was adjusted by 1 mol/L HCl and NaOH and measured with pH meter (Lei Ci made in Shanghai) without buffer before the adsorption. Sodium dihydrogenphosphate (NaH$_2$PO$_4$) was used as the phosphate source. The sub-sample of the solution was collected into the syringe and filtered with 0.25 μm filter disk into a sample tube properly. Then phosphate concentration of the filtered solutions was analyzed according to the ascorbic acid method stated in the standard methods (APHA, 1989) [24].

The adsorptive capacity of La-Ves was defined as:

$$\text{Adsorption capacity} = \frac{V(C_0 - C)}{W}$$

where C_0 is the initial concentration of orthophosphate in bulk solution (mg P/L), C is the equilibrium concentration of orthophosphate in bulk solution (mg P/L), V is the phosphorus solution volume (L) and W is the amount of La-Ves (g).

2.4. Residual lanthanum test

In order to make sure that there was not any considerable damage to the solid, the concentration of residual lanthanum ions in the solutions containing phosphate (1–5 mg P/L) after added La-Ves should be determined. At the end of the adsorption process, the residual solution was collected into the syringe and filtered with 0.25 μm filter disk into a proper sample tube. Concentration of lanthanum in the filtered solutions was analyzed by an inductively coupled plasma atomic emission spectrometer (ICP) (Shimadzu SEQUE-NTIAL PLASMA SPETROMETERICPS-1000II).

2.5. Desorption and regeneration studies

The reusability of La-Ves mainly depends on the ease with which PO$_4^{3-}$ ions get desorbed from used sample. Therefore, 5% HNO$_3$ was used as the regenerant in this study. Recovery test was carried out only for La-Ves samples [14]: 0.3 g La-Ves which had been used once was recollected, then soaked and stirred for 24 h in 100 mg P/L phosphate solution (20 mL) in order to make sure that
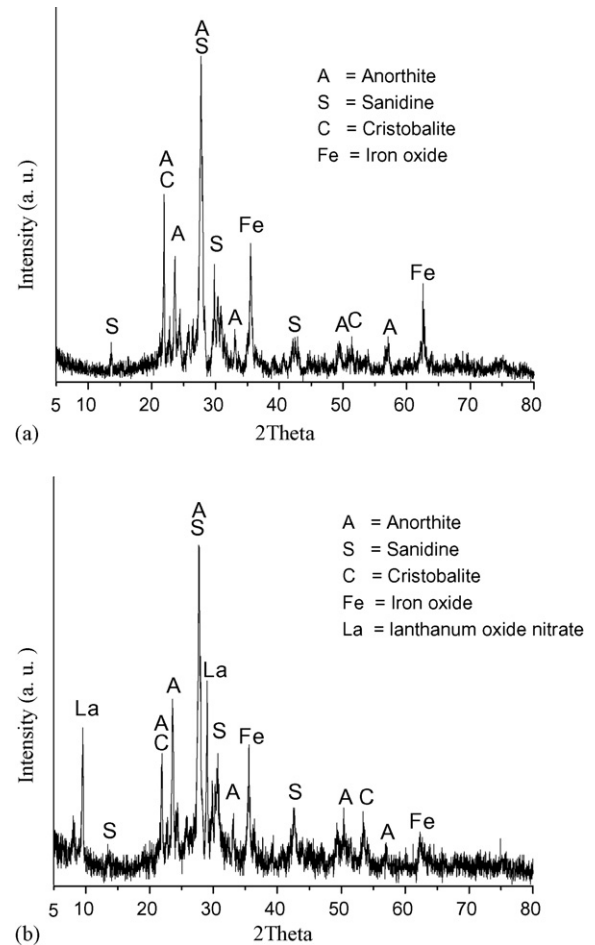

Fig. 1. XRD patterns of vesuvianite (a) and La-Ves (b).

the adsorption–desorption equilibrium have been achieved. The filtered La-Ves was soaked and stirred for 24 h in 25 mL 5% HNO$_3$, then filtered and washed with deionized water to pH ~7, dried at 90 °C for 3 h and calcined at 420 °C for 4 h in air.

3. Results and discussion

3.1. Characteristics of La-Ves

O (45.4%), Si (26.4%) and Al (9.73%) were found to be major elements of undoped vesuvianite measured by XRF. Fe (4.12%), Ca (4.03%), K (3.88%), Mg (2.92%), and Na (2.61%) were also detected. As expected, La (14.2%) was apparent in La-Ves in addition to the above elements. XRD patterns of undoped vesuvianite (Fig. 1a) show the presences of (Ca, Na)(Al, Si)$_2$Si$_2$O$_8$-anorthite, (Na, K)(Si$_3$Al)O$_8$-sanidine, Fe$_3$O$_4$-iron oxide, SiO$_2$-cristobalite. After modified by lanthanum, lanthanum oxide nitrate (LaO(NO$_3$)) was observed (Fig. 1b).

3.2. Effect of different mass ratios of La/Ves at different contact times on adsorption capacity

Fig. 2 describes the effect of different La/Ves mass ratios on adsorption capacity. It was found that the adsorption capacity increased with increasing La/Ves mass ratio. In this study, 0.14 would be the optimum mass ratio used for the removal of phosphate. Undoped vesuvianite only exhibited the adsorption capacity of 0.3 mg P/g, even the contact time was increased to 32 h, the adsorption capacity changed little. This indicates that undoped
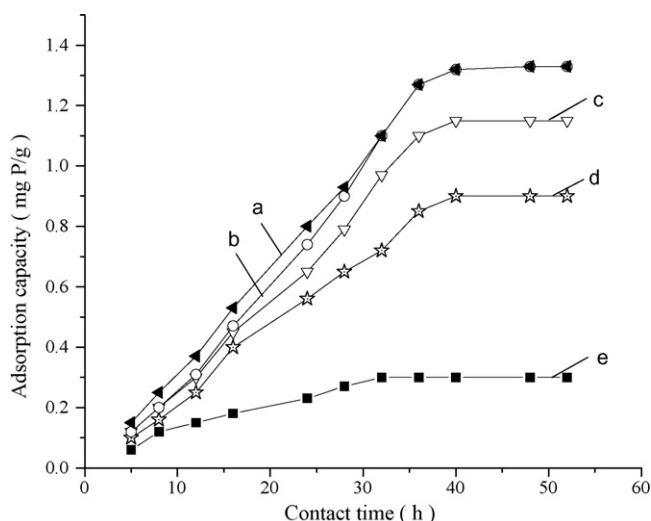
Fig. 2. Effect of different mass ratios of La/Ves at different contact times on adsorption capacity: (a) 0.3 g La0.16-Ves, (b) 0.3 g La0.14-Ves, (c) 0.3 g La0.07-Ves, (d) 0.3 g La0.035-Ves, and (e) 0.3 g undoped vesuvianite; initial P concentration: 1.01 mg P/L; pH 7.1; 1 L solution.

vesuvianite exhibited relatively low adsorption capacity to phosphate. By contrast, after doping with La, the adsorption capacity of La-Ves was significantly improved. Obviously, the precipitation of lanthanum phosphate formed by the reaction of bounded lanthanum in La-Ves with phosphate was a key mechanism for phosphate removal. For example, when the adsorption experiments were conducted for 52 h, La-Ves was taken out and dried at 90 °C for 3 h, which is denoted La-Ves (P). Direct evidence of PO_4^{3-} in La-Ves (P) was obtained by FT-IR (Fig. 3). Compared with those La-Ves without PO_4^{3-}, the absorptions at about 2356 cm^{-1} and 1002 cm^{-1} are attributed to the typical organic phosphate groups on La-Ves(P) [25,26].

According to Fig. 2b, an initial steep increase in the adsorption capacity was observed when the contact time was increased to 40 h for La-Ves. Beyond this contact time, the adsorption capacity increased only a little. The sorption seemed to be influenced by diffusion through rough surface and channels in La-Ves. After 40-h contact time, the P sorption on studied La-Ves remained nearly constant.
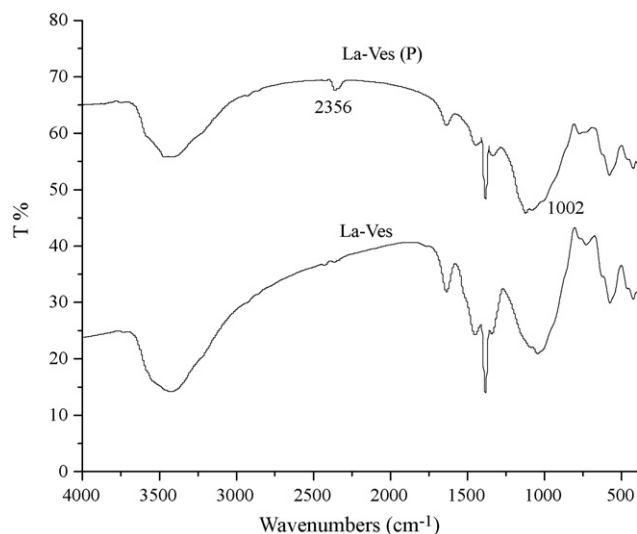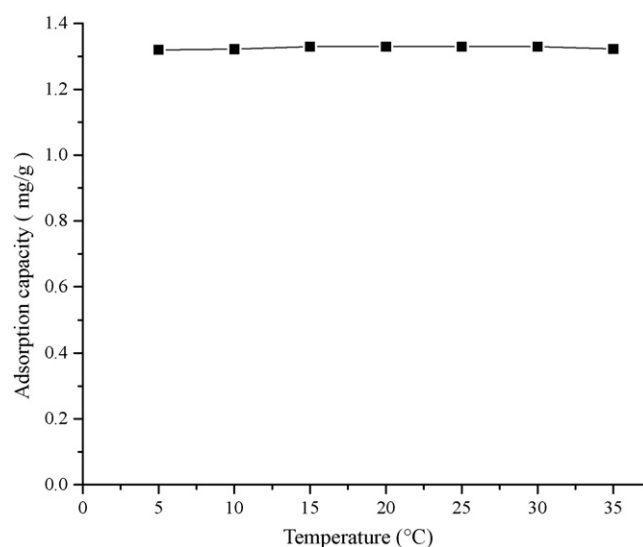

Fig. 3. FT-IR spectra of La-Ves and La-Ves (P).

Fig. 4. Effect of temperature on adsorption capacity: initial P concentration, 1.02 mg P/L; 0.3 g La-Ves; pH 7.1; 1 L solution.

3.3. Effects of temperature and initial P concentration on adsorption capacity and adsorption isotherms

The adsorption capacity as a function of temperature was presented in Fig. 4. It was found that the adsorption capacity could reach about 1.32 mg P/g in the temperature from 20 to 30 °C. This indicates that temperature has little influence on adsorption capacity, and removing phosphate by La-Ves could be carried out at the room temperature.

Equilibrium studies were performed to evaluate the adsorption capacity of La-Ves using different initial concentrations of phosphate (1 mg P/L, 2 mg P/L, 3 mg P/L, 4 mg P/L, and 5 mg P/L). The equilibrium data were analyzed using the following linearized expressions for the Langmuir and Freundlich adsorption isotherms [15]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \left(\frac{1}{Q_0}\right) C_e \tag{1}$$

$$\ln q_e = \ln K_f + \frac{1}{n \ln C_e} \tag{2}$$

where q_e is equilibrium phosphate concentration on adsorbent (mg P/g), Q_0 is a maximum adsorption capacity (mg P/g), K_L is sorption constant (L/mg), C_e is equilibrium phosphate concentration in solution (mg P/L), and K_f and n are the Freundlich exponents.

While the Langmuir isotherm parameters Q_0 and K_L were obtained by plotting C_e/q_e versus C_e, the Freundlich isotherm parameters were obtained by plotting $\ln q_e$ versus $\ln C_e$. The isotherm data were calculated from the least squares method.

Representative plots of adsorption isotherms, q_e versus C_e for La-Ves is described in Fig. 5. It is seen that q_e increased sharply at low equilibrium concentrations, whereas at higher values of C_e, the increase in q_e was gradual. The adsorption parameters and regression coefficients (R^2 values) presented in Table 1, indicated that the

Table 1
Comparison of Langmuir and Freundlich adsorption isotherm models.

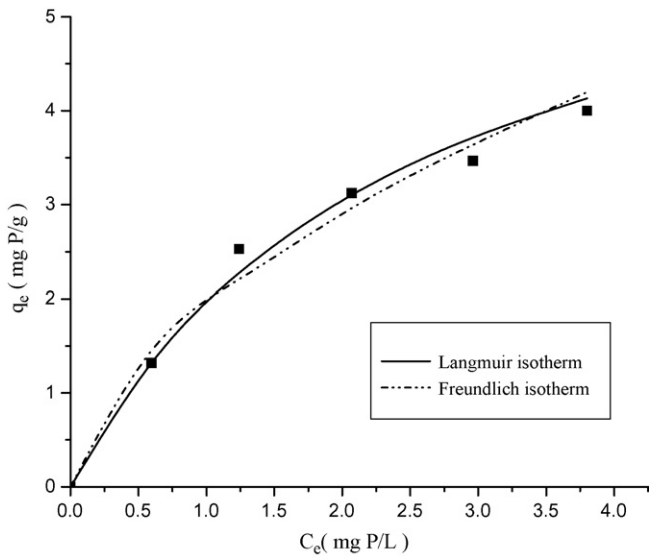| Model					
Langmuir			Freundlich		
X_m (mg P/g)[a]	K_L (L/mg)[a]	R^2 [a]	K_f (mg P/g)[a]	n [a]	R^2 [a]
6.703	0.447	0.995	1.964	1.629	0.984

[a] Parameters.

Fig. 5. The Langmuir and Freundlich models simulated equilibrium sorption isotherms over La-Ves: initial P concentration: 1.02 mg P/L, 2.03 mg P/L, 3.08 mg P/L, 3.98 mg P/L, and 5.03 mg P/L; 0.3 g La-Ves; pH 7.1; 1 L solution.

adsorption equilibrium data over the concentration range used in this investigation fitted better the Langmuir model than the Freundlich model, and the maximum adsorption capacity of La-Ves was calculated to be 6.7 mg P/g. It exhibited faster adsorption kinetics as well as higher adsorption capacities than acid-thermal treated red mud [12] and Fe(III)/Cr(III) hydroxide did [27].

3.4. Residual lanthanum ions

To determine the concentration of the loosely bound La in the treated solution, it was analyzed by ICP. As expected, the concentration of residual lanthanum ions is very low. The concentration of residual lanthanum ions was 0.26 mg/L and 0.09 mg/L when the initial concentration of phosphate solution was 1 mg P/L and 2 mg P/L respectively. This indicated most of lanthanum ions were bounded in the framework of La-Ves. Considering the residual lanthanum ions and the formation of $LaPO_4$ on La-Ves, La-Ves could be considered an environment-friendly material for the removal of phosphate. The fact that there was not any residual lanthanum ions in solution at initial concentration ≥ 3 mg P/L implies that phosphate has reacted with almost all of the loosely bound La since the amount of residual lanthanum ions was very small.

3.5. Effect of pH on adsorption capacity

The effect of pH on adsorption capacity was also investigated and depicted in Fig. 6. It reveals that adsorption capacity changed a little when the pH from 3 to 11 and it tended to approach a maximum value (about 1.32 mg P/g) at pH between 6 and 9. A remarkable observation from the pH tests was that, adsorption capacity decreased with increasing pH at pH > 11, which can be attributed to the competition between hydroxyl ions and phosphate ions for adsorption sites. Therefore, pH variation between 3 and 13 was found to have a small effect on adsorption capacity.

3.6. The application of La-Ves in the treatment of polluted water from a river into Lake Dianchi

In order to extend the possible applications of La-Ves, further tests were carried out using polluted water from a river into Lake Dianchi (the initial phosphate concentration was 0.94 mg P/L).
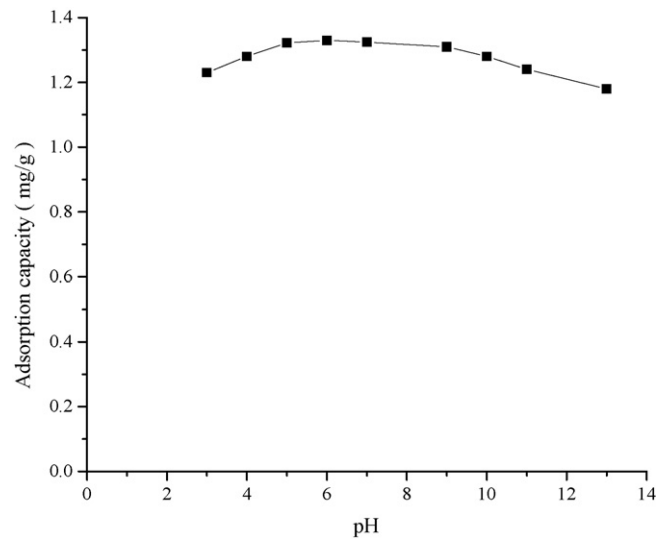

Fig. 6. Effect of pH on adsorption capacity: initial P concentration, 0.995 mg P/L; 0.3 g La-Ves; 1 L solution.

Under natural pH (pH 8), the variation of adsorption capacity with contact time over La-Ves is shown in Fig. 7. It is seen that La-Ves was also effective in removing phosphate (adsorption capacity was 1.31 mg P/g) after 52 h. However, the contact time for this polluted water is a little longer than that for the prepared phosphate containing water using NaH_2PO_4 as the phosphate source (40 h), since there were more organic and inorganic pollutants in the polluted water.

3.7. Adsorption capacity using regenerated La-Ves

The variation of adsorption capacity of regenerated La-Ves with contact time is shown in Fig. 8. Compared with fresh La-Ves, an initial steep increase of adsorption capacity was observed when the contact time was ≤ 48 h. Beyond this contact time, there was only slight increase of adsorption capacity, and it seemed leveled off even when the contact time was up to 72 h (the adsorption capacity was 1 mg P/g). This suggests that La-Ves can be recycled at least once without losing its activity to a greater extent. The mechanism for the regeneration process is depicted in Scheme 1.
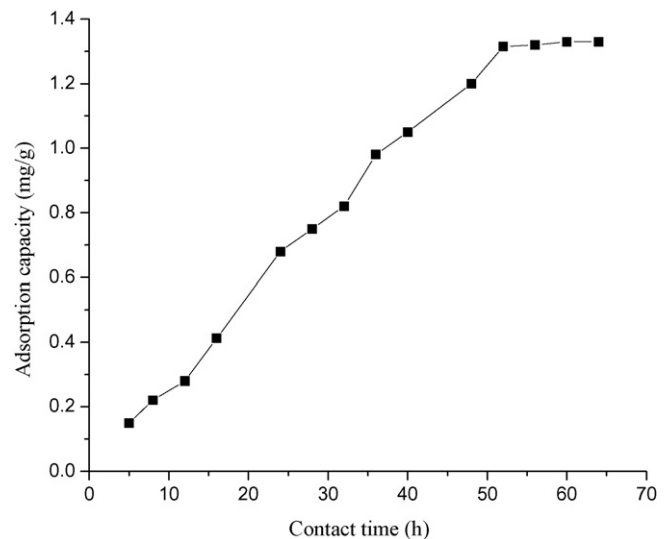

Fig. 7. Phosphate removal in polluted water from a river into Lake Dianchi over La-Ves: initial P concentration, 0.94 mg P/L; 0.3 g La-Ves; pH 8; 1 L solution.
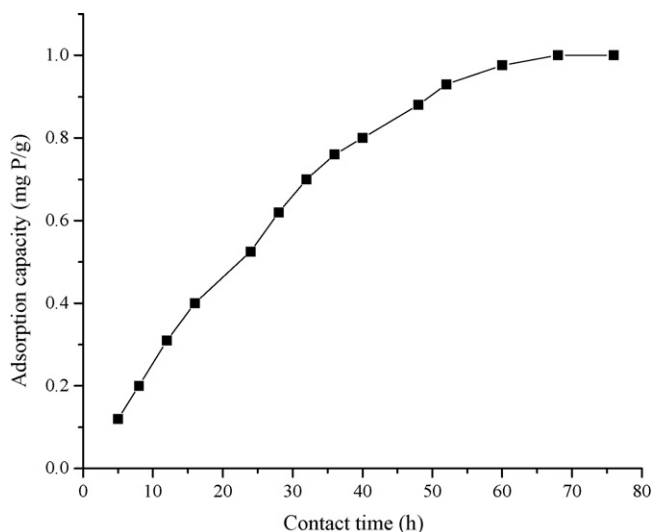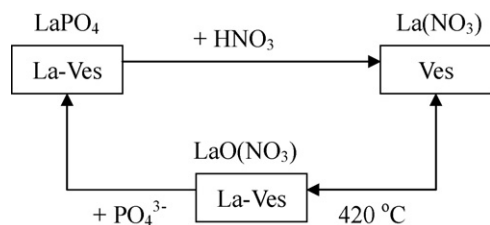
Fig. 8. Phosphate removal using regenerated La-Ves: initial P concentration, 0.99 mg P/L; 0.3 g La-Ves; pH 7.1; 1 L solution.

Scheme 1. The mechanism for the regeneration process for La-Ves.

4. Conclusions

In this study, vesuvianite was modified by lanthanum and the properties of La-Ves as an adsorbent for phosphate removal were examined. La-Ves has been demonstrated to be able to efficiently reduce the phosphate in both standard phosphate solutions and polluted water. The adsorption capacity of La-Ves for the removal of phosphate increased with increasing La/Ves mass ratio, and it changed a little when the pH from 3 to 11. When the initial phosphate concentration was 1 mg P/L, the adsorptive capacity rate would be 1.32 mg P/g La-Ves (La/Ves mass ratio ≥0.14) at pH between 6 and 9 after 40 h. The Langmuir equation better fitted the sorption equilibrium data over the concentration range used in this investigation than the Freundlich equation did. In addition, the floating property of La-Ves makes it easily recycled and without losing its activity to a greater extent. It was also found that La-Ves was an environment-friendly adsorbent.

Acknowledgements

References

[1] A. Ugurlu, B. Salman, Phosphorus removal by fly ash, Environ. Int. 24 (1998) 911–918.
[2] M.A. Anderson, A.J. Rubin, Adsorption of Inorganics at Solid–liquid Interfaces, Ann Arbor Science Publishers Inc., 1981, pp. 1–80.
[3] E. Galarnaeau, R. Gehr, Phosphorus removal from wastewaters: experimental and theoretical support for alternative mechanisms, Water Res. 31 (1997) 328–338.
[4] W. Tang, O. Shima, A. Ookubo, K. Ooi, A kinetic study of phosphate adsorption by boehmite, J. Pharm. Sci. 86 (1997) 230–235.
[5] B.B. Johnson, A.V. Ivanov, O.N. Antzutkin, W. Forsling, ^{31}P nuclear magnetic resonance study of the adsorption of phosphate and phenyl phosphates on γ-Al$_2$O$_3$, Langmuir 18 (2002) 1104–1111.
[6] Z. Hongshao, R. Stanforth, Competitive adsorption of phosphate and arsenate on goethite, Environ. Sci. Technol. 35 (2001) 4753–4757.
[7] S. Lin, H. Kao, C. Cheng, R. Juang, An EXFAS study of the structures of copper and phosphate sorbed onto goethite, Colloids Surf. A 234 (2004) 71–75.
[8] R. Juang, J. Chung, Equilibrium sorption of heavy metals and phosphate from single- and binary-sorbate solutions on goethite, J. Colloid Interf. Sci. 275 (2004) 53–60.
[9] Tsitouridou, J.A. Georgiou, A contribution to the study of phosphate sorption by three Greek fly ashes, Toxicol. Environ. Chem. 17 (1987) 129–138.
[10] H. Yamada, M. Kayama, K. Saito, M. Kara, A fundamental research on phosphate removal by using slag, Water Res. 20 (1986) 547–557.
[11] K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, J. Hazard. Mater. 139 (2007) 447–452.
[12] W. Huang, S. Wang, Z. Zhu, L. Li, X. Yao, V. Rudolph, F. Haghseresht, Phosphate removal from wastewater using red mud, J. Hazard. Mater. 158 (2008) 35–42.
[13] E.W. Shin, J.S. Han, M. Jang, S.H. Min, J.W. Park, R.M. Rowell, Phosphate adsorption on aluminum-impregnated mesoporous silicates: surface structure and behavior of adsorbents, Environ. Sci. Technol. 38 (2004) 912.
[14] E. Ou, J. Zhou, S. Mao, J. Wang, F. Xia, L. Min, Highly efficient removal of phosphate by lanthanum-doped mesoporous SiO$_2$, Colloids Surf. A: Physicochem. Eng. Aspects 308 (2007) 1–3.
[15] P. Pengthamkeerati, T. Satapanajaru, P. Chularuengoaksorn, Chemical modification of coal fly ash for the removal of phosphate from aqueous solution, Fuel 87 (2008) 2469–3247.
[16] H. Ye, F. Chen, Y. Sheng, G. Sheng, J. Fu, Adsorption of phosphate from aqueous solution onto modified palygorskites, Sep. Purif. Technol. 50 (2006) 283–290.
[17] K.A. Krishnan, A. Haridas, Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith, J. Hazard. Mater. 152 (2008) 527–535.
[18] Z. Qian, Vesuvianite and the research development of its exploitation and utilization, J. Mineral Petrol. 2 (1998) 110–114 (in Chinese).
[19] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock-forming Minerals, 2nd ed., Long-man, New York, 1992.
[20] L.A. Groat, F.C. Hawthorne, T.S. Ercit, The chemistry of vesuvianite, Can. Mineral. 30 (1992) 19–48.
[21] J. Wang, The exploitation of vesuvianite in Tengchong, Stone 12 (2000) 37–39 (in Chinese).
[22] S.A. Wasay, M.J. Haron, S. Tokunaga, Adsorption of fluorine, phosphorus and arsenate irons on lanthanum-impregnated silica gel, Water Environ. Res. 68 (1996) 295–300.
[23] S. Tokunaga, T. Hakuta, S.A. Wasay, Treatment of waters containing hazardous anions using rare-earth based materials, J. Natl. Inst. Mater. Chem. Res. 7 (1999) 291–334.
[24] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA, 1998.
[25] H.K. Jung, J.S. Oh, S.I. Seok, T.H. Lee, Preparation and luminescence properties of LaPO$_4$: Er, Yb nanoparticles, J. Lumin. 114 (2005) 307–313.
[26] D.S. Soejoko, M.O. Tjia, Infrared spectroscopy and X-ray diffraction study on the morphological variations of carbonate and phosphate compounds in giant prawn (*Macrobrachium rosenbergii*) skeletons during its moulting period, J. Mater. Sci. 38 (2002) 2087–2093.
[27] C. Namasivayam, K. Prathap, Recycling Fe(III)/Cr(III) hydroxide, an industrial solid waste for the removal of phosphate from water, J. Hazard. Mater. 123 (2005) 127–134.