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Preparation and adsorption of phosphorus by new heteropolyacid salt–lanthanum oxide composites

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ABSTRACT

In this article, we reported a new method in which molybdenum heteropolyacid salt was selected to mix with lanthanum oxide and bentonite, respectively, and the dipping method was used to prepare the new composites of heteropolyacid salt–lanthanum oxide, heteropolyacid salt–bentonite, and heteropolyacid salt–lanthanum oxide–bentonite. We observed that the composites have a better removal effect for phosphorus by control of the ratio and calcination temperature. The effect of quantity, adsorption time, phosphorus wastewater concentration, and pH value of composites on phosphorus adsorption was studied. We also found that the removal rate of phosphorus by the composite of heteropolyacid salt–lanthanum oxides increases up to 99.1% under the condition of 1:1 mass ratio and 500°C of calcination temperature. IR and XRD studies suggest that molybdenum heteropolyacid salt has been loaded to lanthanum oxide carrier successfully and heteropolyacid salt keeps the original Keggin structure. Heteropolyacid salt–lanthanum oxide has a good adsorption effect on phosphorus under the condition of 0.15 g of the composite, 90 min of adsorption time, phosphorus concentration of 50 mg L^{-1}, and pH value of 3. The adsorption of phosphorus corresponds with the Langmuir isotherm model and Lagergren first-order kinetics equation. Therefore, the composite has excellent absorption ability and was competent in removing phosphorus with a low concentration from aqueous solution. It could be a great potential adsorbent for the removal of phosphorus in lakes, rivers, and reservoirs.

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1. Introduction

Nitrogen and phosphorus play very important roles in the eutrophication pollution of lakes. Previous studies have shown that more than 80% of the phosphorus in lakes, rivers, and reservoirs come from sewage discharge [1]. As a result, the development of economic and efficient removal methods of phosphorus is now urgently needed. Current methods for the removal of phosphorus from wastewater at homeland and abroad fall into two categories [2]: physico-chemistry and biological method. The physico–chemical method can be divided into chemical precipitation, crystallization, adsorption, and electrodialysis. The process of biological phosphorus removal method is complex and a grand challenge to ensure water quality. The chemical sludge of chemical precipitation is difficult to handle and results in many other defects [3–7]. Therefore, the adsorption method has drawn much attention due to its less quantity of sludge [8], low cost, stable treatment effect, and especially suitable for treating the wastewater of low concentration. Current studies on phosphorus removal at homeland and abroad by adsorption mainly focus on improving the performance of the adsorbent. The existing adsorbents are natural materials, wastes, activated alumina, modified substances, porous materials, and synthetic adsorbent. But the adsorption capacity of these adsorbents on phosphorus removal has not been good enough till now, and most of the adsorbent has a relatively short lifespan. Therefore, the preparation of excellent adsorbents for phosphorus removal has become essential [9]. Lanthanum oxide [10] has advantages of high dispersion, large specific surface area, and strong chemistry activity; so, it has attracted much attention for the reparation of new adsorbents, the adsorption capacity of pure lanthanum oxide on phosphorus still has some drawbacks. Bentonite is often used as adsorbents because of its peculiar properties such as adsorption capacity, swelling behavior, anisotropic shape, reactive surfaces, and high cation exchange capacity. It can also be used as catalyst and catalyst support in the field of photocatalysis research.

Therefore, in this work, we developed a new method in which molybdenum heteropolyacid salt [11] was selected to mix with lanthanum oxide and bentonite [12], respectively, and the dipping method was used to prepare a composite to remove the phosphorus in wastewater, which extended the adsorption characteristic of the lanthanum oxide and combined with the advantages of the heteropolyacid salt. Our study shows the composite improves significant adsorption properties of phosphorus.

2. Experimental section

2.1. Preparation of $(NH_4)_4\,[Mo_8O_{24}(C_3H_2O_4)_2]\cdot 4H_2O$ [13] and screening of composite materials

The molybdenum heteropolyacid salt $(NH_4)_4[Mo_8O_{24}(C_3H_2O_4)_2]\cdot 4H_2O$ was synthesized with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, NH_4VO_3, and $C_3H_4O_4$ as raw materials. 1.8 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.5 g of NH_4VO_3 were dissolved in 25 mL water. When the solution became clear, 3.6 g of $C_3H_4O_4$ was added to the solution. The mixture was heated at 80℃ for 40 min, and then cooled down to room temperature, and lasted for 3 d until the small yellow crystals were obtained, then dried in the oven, and grinded.

Molybdenum heteropolyacid salt was mixed with lanthanum oxide and bentonite, respectively, by the dipping method with a mass ratio of 1:1. On filtration, the mixtures were dried and baked at 300, 400, and 500℃ for 3 h to prepare the composites of heteropolyacid salt–lanthanum oxide, heteropolyacid salt–bentonite, and heteropolyacid salt-lanthanum oxide–bentonite. Taking a certain amount of composites (heteropolyacid salt–lanthanum oxide, heteropolyacid salt–bentonite, and heteropolyacid salt–lanthanum oxide–bentonite) used for the adsorption of phosphorus, the removal effect of phosphorus was optimized as adsorbents according to the removal rate of phosphorus.

2.2. Characterization of composite materials

XRD was performed on a Japans X'pert diffractometer equipped with Ni-filtered Cu–Kα radiation source ($\lambda = 0.15418$ nm). The X-ray tube was operated at 40 kV and 40 mA. IR characterization of the composites was carried out using NICOLET IS10 type on the Fourier infrared spectrometer for KBr tabletting method to test at room temperature.

2.3. Sorption capacity

0.15 g composites and 50 mL (50 mg/L) phosphorus solution were shaken on the thermostatic oscillator flask for 1 h at room temperature. Then the solution was

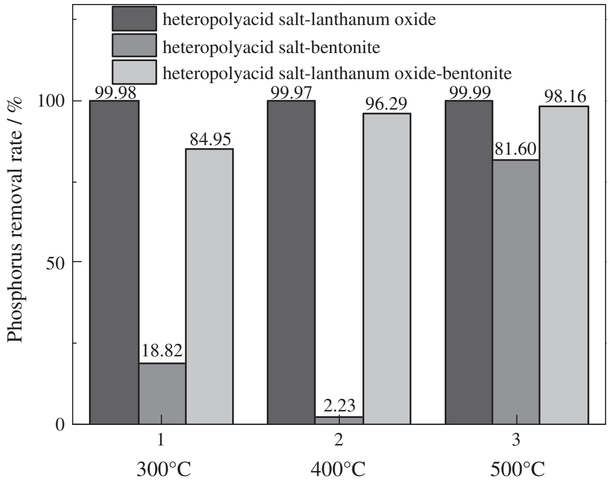

Fig. 1. Effect of different composite materials on the removal rate of phosphorus. (Initial phosphate concentration of 50 mg/L, adsorbent dosage 3.0 g/L).

centrifuged and the absorbance was measured. The concentrations of phosphate were analyzed by the Mo–Sb anti-spectrophotometric method [14]. The phosphate removal efficiency (R, %) and adsorption quantity (Q, mg/g) were calculated as in Eqs. (1) and (2).

$$R = (C_0 - C_t) \times 100\%/C_0 \tag{1}$$

$$Q = (C_0 - C_t)\, V\, /1000 \times m \tag{2}$$

Here C_0 (mg/L) and C_t (mg/L) are the initial and t time concentrations of the phosphate, respectively, V is the phosphorus solution volume (L), and m is the adsorbent mass (g).

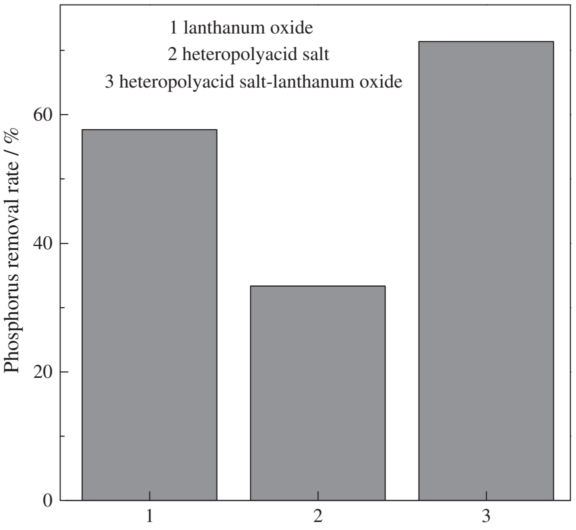

Fig. 2. Effect of different adsorbents on phosphorus removal rate. (Initial phosphate concentration of 50 mg/L, adsorbent dosage 3.0 g/L and temperature = 20±0.5℃).

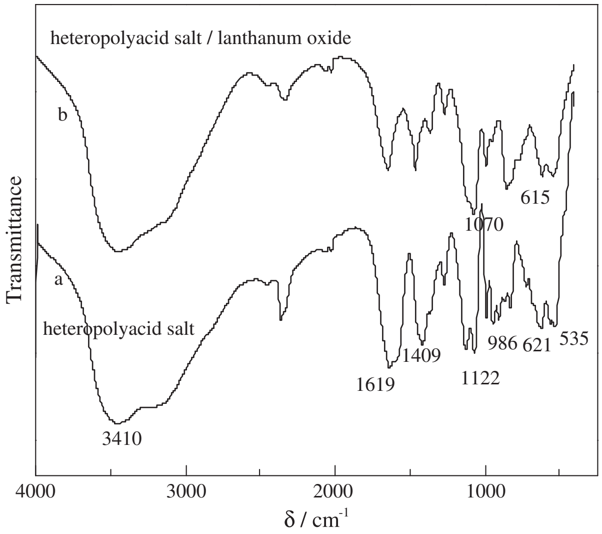

Fig. 3. IR spectra of heteropolyacid salt and heteropolyacid salt–lanthanum oxide.

3. Results and discussion

3.1. Selection of composite materials

3.1.1. Composites of the heteropolyacid salt–lanthanum oxide

In order to compare the removal rate of phosphorus with different composites of heteropolyacid

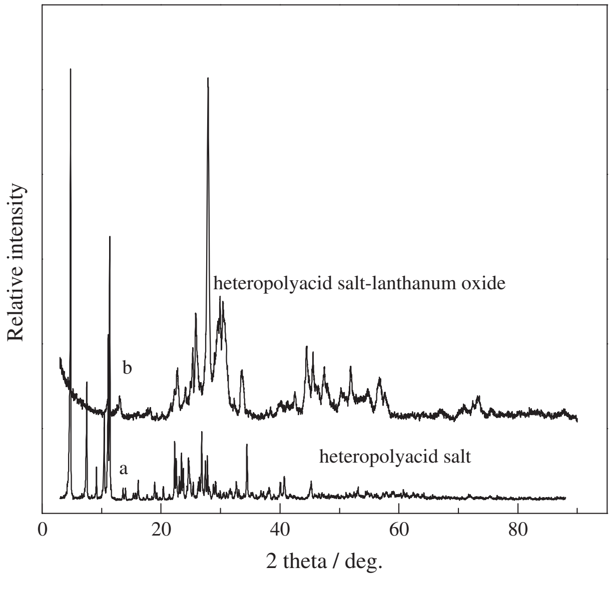

Fig. 4. XRD spectra of heteropolyacid salt and heteropolyacid salt–lanthanum oxide.

salt–lanthanum oxide, heteropolyacid salt–bentonite, and heteropolyacid salt–lanthanum oxide–bentonite on phosphorus adsorption capacity, the removal rate of composites on phosphorus was measured in the same process. As shown in Fig. 1, the composites of heteropolyacid salt–lanthanum oxide, which are prepared under the condition of 500℃ of calcination temperature, have a higher removal rate for phosphorus than others, and its removal rate increases to 99.1%.

3.1.2. Adsorption

The different adsorbents of lanthanum oxide, heteropolyacid salt, and heteropolyacid salt–lanthanum oxide on phosphorus removal rate were measured in the same process. As shown in Fig. 2, heteropolyacid salt and lanthanum oxide are ineffective on phosphorus adsorption, and the removal rate only reaches 33.3 and 57.7%, respectively. But the phosphorus removal rate of heteropolyacid salt–lanthanum oxide is up to 71.4%. The results indicate that the phosphorus removal of the heteropolyacid salt–lanthanum oxide has been significantly enhanced.

3.2. IR and XRD analysis

3.2.1. IR analysis

IR was used to determine the primary structure of heteropolyacid compounds. Fig. 3(a) shows that

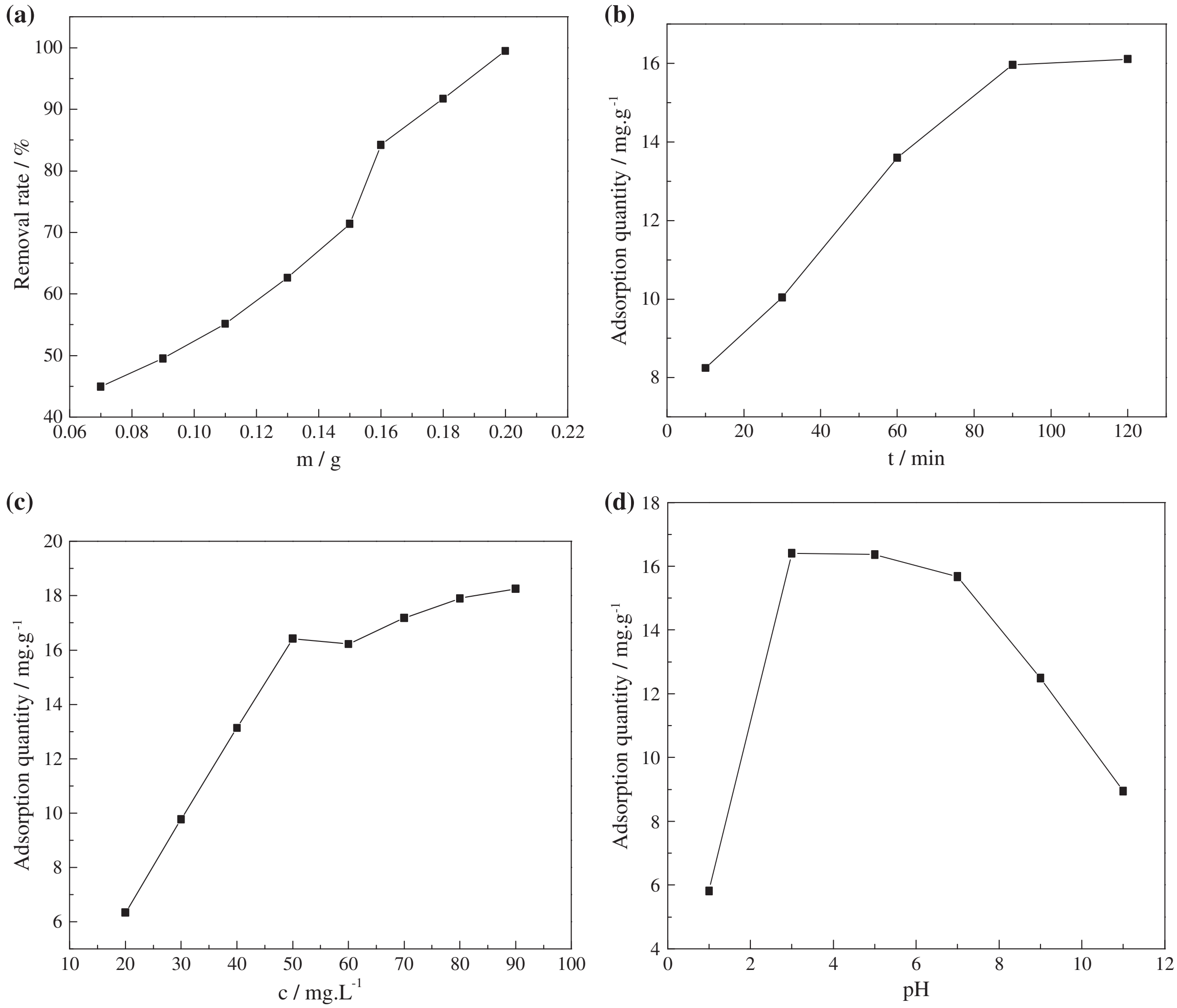

Fig. 5. Effect of different experimental conditions on phosphorus adsorption. (a) Effect of different composites quantity on Phosphorus removal rate, (b) effect of adsorption time on phosphorus adsorption, (c) effect of phosphorus wastewater concentrationon on phosphorus adsorption, and (d) effect of pH values on phosphorus adsorption.

3,410 cm^{-1} is H_2O's H–O–H stretching vibration peak. The peaks of 1,409.59 and 1,619.35 cm^{-1} are the absorption peaks of carboxyl symmetric stretch and anti-symmetric stretch. The peak of 1,122.73 and 986.95 cm^{-1} is the absorption peak of Mo–O–Mo asymmetric vibration. The absorption peaks of Mo–O–Mo symmetric vibration are at 621.63 and 535.37 cm^{-1}, respectively. According to Fig. 3(b), the absorption peak of Mo–O–Mo asymmetric and symmetric vibrations remains unchanged after loading lanthanum oxide, which indicates that molybdenum heteropolyacid salt was loaded to lanthanum oxide successfully, and has kept the original Keggin structure for heteropolyacid salt. But the peak of Mo–O–Mo asymmetric vibration absorption was blue shifting from 1,122.73 to 1,070.98 cm^{-1}, and the absorption peak of Mo–O–Mo symmetric vibration was blue shifting from 621.63 to 615.43 cm^{-1}. This indicates that it might result from hydrogen bonding in the process of the load.

3.2.2. XRD analysis

The XRD spectra of heteropolyacid salt and heteropolyacid salt–lanthanum oxide are shown in Fig. 4. The diffraction characteristic peak of heteropolyacid salt in Fig. 4(a) and (b) at 25.27°, 27.47°, 41.21°, 47.89°, and 54.31° remained the same. This indicates that molybdenum heteropolyacid salt has been loaded to lanthanum oxide successfully, and heteropolyacid salt keeps the original Keggin structure. The diffraction characteristic peak of heteropolyacid salt–lanthanum oxide appeared as weak peaks at the 2θ peak of 53.65°, 47.36°, and characteristic peaks of lanthanum oxide were indicated after heteropolyacid salt–lanthanum oxide was composited.

3.3. Adsorption properties of phosphorus

3.3.1. Effect of different experimental conditions on phosphorus adsorption capability

In order to investigate the effect of composites of heteropolyacid salt–lanthanum oxide on phosphorus adsorption on the amount of composite materials, adsorption time, initial concentration of phosphorus, and different pH values were studied, and the result is shown in Fig. 5(a), (b), (c), and (d).

As shown in Fig. 5(a), the phosphate removal rate has increased and the effective removal of composite materials has been enhanced with an increase in the composites' mass from 0.07 to 0.15 g. The removal of phosphate has increased quickly when the composites' dosage exceeds 0.15 g. Given the costs, the better dosage of the composite material was chosen as 0.15 g. Furthermore, the adsorption quantity increases and the adsorption effect enhances with an increase in the oscillation time from 10 to 90 min in Fig. 5(b). The adsorption quantity didn't appear to add up as adsorption time when increasing above 90 min. This is mainly because with an increase in the adsorption, adsorbate shifted gradually from the surface to inside pores, and the adsorption became slow, and the adsorption capacity had a little change because of the increase in the mass transfer resistance. Different phosphorus wastewater concentrations of phosphorus adsorption capacity relations are shown in Fig. 5(c). Adsorption quantity increases gradually and the adsorption effect enhances with an increase in the phosphorus concentration of wastewater with the concentration range from 20 to 90 mg L^{-1}. While

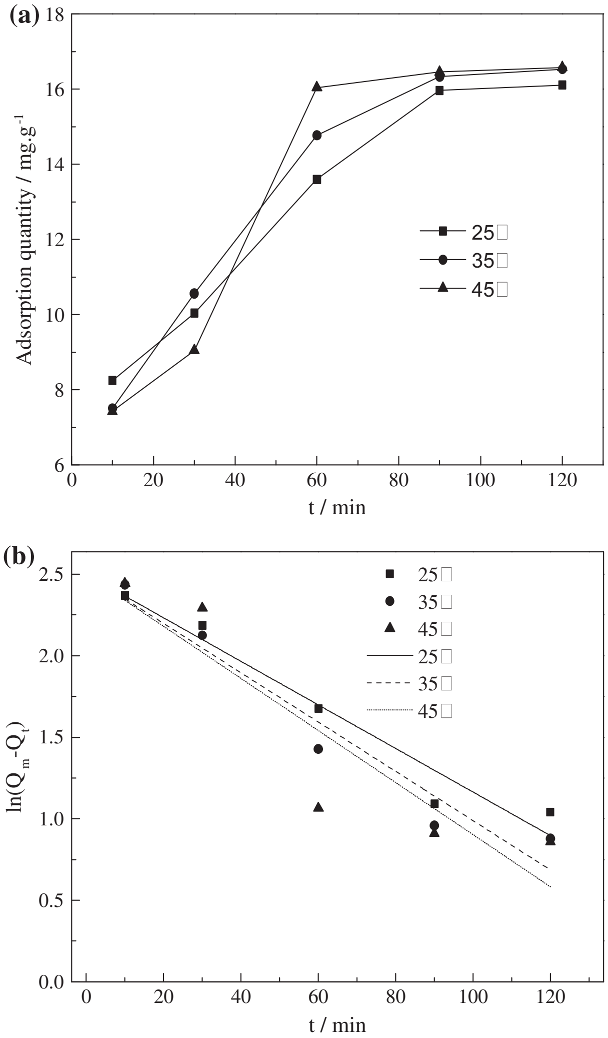

Fig. 6. (a) Effect of adsorption temperature on phosphorus adsorption and (b) dynamic adsorption line.

Table 1
The Lagergren first-order kinetics equation, R, and k_a of different temperatures of heteropolyacid salt/lanthanum oxide on phosphorus adsorption

T/℃	Fitting equation	R	k_a
25℃	$\ln(A_m - A_t) = -0.0134\,t + 2.5040$	0.9759	0.0134
35℃	$\ln(A_m - A_t) = -0.0152\,t + 2.5077$	0.9709	0.0152
45℃	$\ln(A_m - A_t) = -0.0161\,t + 2.5144$	0.9127	0.0161

phosphorus concentration was larger than 90 mg L^{-1}, the adsorption quantity no longer increases, which is due to the fact that composites' adsorption of phosphorus is saturation. Different pH values shown in Fig. 5(d) indicate that adsorption capacity increases gradually between the pH of 1 and 3, and the adsorption effect enhances between the pH of 3 and 5. When the pH is 7, adsorption quantity no longer increases, and adsorption capacity decreases obviously. If pH is lower than 7, the phosphorus species is H_3PO_4 and $H_2PO_4^-$ in the wastewater solution, and they form electrically neutral complexes with the surface hydroxyl of composites, which may be beneficial for the adsorption of phosphate in wastewater. When the pH is above 7, the forms of phosphorus [15] are HPO_4^{2-} and PO_4^{3-}, and the formed complexes are charged negatively. Because of the electrostatic repulsion, the adsorption of phosphorus on adsorbent surface reduces in wastewater.

3.3.2. Adsorption mechanism

3.3.2.1 Adsorption kinetics. The relationship of adsorption quantity and time is shown in Fig. 6(a). According to Fig. 6(a), linear regression of the adsorption rate curves is fitted with the Lagergren first-order kinetics equation:

$$\ln(Q_m - Q_t) = \ln Q_m - k_a t \tag{3}$$

Here, Q_m (mg/g) and Q_t (mg/g) are the adsorption capacities at equilibrium and at time t, respectively, and k_a is the rate constant. The relation curve of ln $(Q_m - Q_t)$ and t is displayed as Fig. 6(b) shows.

As shown in Fig. 6(b), with different temperatures, phosphorus adsorption is fit for the Lagergren first-order kinetic equation, and the values obtained are listed in Table 1.

By Arrhenius formula [16]: $\ln k_{a2}/k_{a1} = E_a/R\,(1/T_1 - 1/T_2)$, the adsorption activation energy E_a was calculated as 9.616 kJ mol^{-1} (25, 35℃) and 4.683 kJ mol^{-1} (35, 45℃). The E_a values are usually between 40 and 400 kJ mol^{-1}, which have a great influence on the reaction rate. When E_a is less than 40 kJ mol^{-1}, the reaction can be instantaneous. So, this experiment reaction was conducted at room temperature.

3.3.2.2. Adsorption isotherm. For the adsorption, the most commonly used are adsorption isotherms such as Langmuir and Freundlich isotherm.

Langmuir adsorption isotherm equation [17]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{4}$$

Freundlich adsorption isotherm equation [17]:

$$\ln Q_e = \frac{1}{n}\ln C_e + \ln K_f \tag{5}$$

In the equation, Q_e (mg/g) and Q_m (mg/g) are the sorption capacities at equilibrium and saturation, respectively, and K is the adsorption equilibrium constant. Under the optimum conditions, heteropolyacid salt–lanthanum oxide on the phosphorus adsorption data was linearly fitted according to the Langmuir and Freundlich isothermal adsorption isotherm formula. The adsorption isotherm equation obtained is shown in Table 2.

According to Table 2, the composite of heteropolyacid salt–lanthanum oxide on the phosphorus adsorption has been described well by the Langmuir adsorption model. In different ranges of researched concentration, it indicates that the phosphorus adsorbent adsorption capacity has been increased with

Table 2
The Langmuir and Freundlich isothermal adsorption model parameters of heteropolyacid salt–lanthanum oxide on phosphorus adsorption

Langmuir adsorption model				Freundlich adsorption model			
Fitting equation	Q_m/mg g^{-1}	K_L	R	Fitting equation	n	K_f/mg g^{-1}	R
$C_e/Q_e = 0.0528\,C_e + 0.0401$	18.94	1.316	0.9977	$\ln Q_e = 0.1863\ln C_e + 2.3988$	5.37	11.01	0.7094

an increase in the equilibrium concentration of phosphorus. When the equilibrium concentration is above a certain value, the adsorption reaches equilibrium and approaches saturation.

4. Conclusions

Heteropolyacid salt was selected to mix with lanthanum oxide and bentonite, respectively, and the dipping method was used to prepare the new composites of heteropolyacid salt–lanthanum oxide, heteropolyacid salt–bentonite, and heteropolyacid salt–lanthanum oxide–bentonite. The composite of heteropolyacid salt–lanthanum oxide has shown a good removal effect for phosphorus under the conditions of 1:1 mass ratio and 500℃ of calcination temperature, and its removal rate increases to 99.1%. IR and XRD characterizations suggest that heteropolyacid salt has been supported by lanthanum oxide carrier successfully, and heteropolyacid salt keeps the original Keggin structure. The quantity, adsorption time, phosphorus wastewater concentration, and pH value of composites on phosphorus adsorption were studied. The results show that heteropolyacid salt–lanthanum oxide has good adsorption effect on phosphorus under the condition of 0.15 g of composite, 90 min of adsorption time, phosphorus concentration of 50 mg L^{-1}, and a pH value of 3. The adsorption of phosphorus corresponds with the Langmuir isotherm model and Lagergren first-order kinetics equation.

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References

[1] W. Hongbin, Y. Min, W. Jiong, Phosphorus adsorption properties of adsorbent of load the lanthanum humic acid, Rare Metal 5 (2002) 356–359.

[2] Y. Yongzhu, J. Yingxiang, Z. Lili, L. Yanbing, Phosphorous removal from wastewater by iron- lanthanum based alloy oxides and their regeneration, Chinese J. Environ. Eng. 1 (2014) 236–240.

[3] L. Chao, Z. Banghui, A review on removing phosphorus from wastewater by zeolite, Guangdong Chem. Ind. 3 (2010) 28–30.

[4] T. Hano, H. Takanashi, M. Hirata, K. Urano, S. Eto, Removal of phosphorus from wastewater by activated alumina adsorbent, Water Science and Technology 35 (1997) 39–46.

[5] W. Guangwei, Q. Liping, Z. Shoubin, Development of Phosphorus removal from wastewater and phosphorus recovery, Technol. Water Treat. 3 (2010) 17–21.

[6] W. Fang, W. Cheng, Development of eutrophication of lakes *in situ* biological treatment technology, Environ. Sci. Surv. 1 (2010) 49–52.

[7] X. Hongsheng, X. Xin, Phosphorus removal from wastewater technology and progress analysis, Environ. Sci. Mange. 1 (2006) 125–128.

[8] L. Yikai, W. Deyi, Z. Xiangyong, K. Hainan, Effects of several common ions on phosphate removal by zeolite synthesized from fly ash, Environ. Pollut. Control 11 (2008) 49–57.

[9] C. Xiaojuan, X. Juqiang, The research dynamic of phosphorus removal from wastewater, Gansu Sci. Technol. 3 (2004) 102–103.

[10] L. Fang, Z. Fengping, J. Yingxiang, H. Jintao, Research on the phosphate removal by consolidated and oxidized lanthanum, Ind. Water Treat. 6 (2010) 11–14.

[11] Yu Xinwu, L. Guosong, C. Li, L. Yinhua, The preparation and properties of contain titanium molybdenum tungsten heteropoly acid salt catalyst, Rare Metal 6 (2003) 839–841.

[12] H. Wanfeng, Y. Min, L. Shiyun, F. Guiquan, W. Hongbin, On the adsorption of *Lonicera* on bentonite, J. Yunnan Nationalities Univ. (Natural Sci. Ed.) 4 (2008) 343–346.

[13] A.S. Özcan, E.M. Oncu, A. Ozcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto BTMA–bentonite, Colloid Surf., A: Physicochem. Eng. Aspects 266 (2005) 73–81.

[14] State Environmental Protection Administration "Water and Wastewater Monitoring and Analysis Methods", Water and Wastewater Monitoring and Analysis Methods, China Environmental Science Press, Beijing, 1998.

[15] L. Yanqin, Z. Li, H. Zhaoju, Z. Hua, L. Xiaoxia, Phosphorus adsorption from wasterwater by iron-oxide-coated-zeolite, Environ. Eng. 4 (2015) 48–52.

[16] S. Zhen hua, W. Xiao han, Z. Xiao jun, W. Yong, Effects of pyrolysis conditions on gasification reactivity and methods acquiring kinetic parameters of isothermal gasification for biomass char, Adv. New Renewable Energy 3 (2015) 14–20.

[17] L. Haining, C. Jing, L. Qiumei, F. Xiang, W. Zhuo, Z. Gaosheng, Adsorptive removal of phosphate from water using Fe-Mn binary oxide coated sea sand, Acta Scientiae Circumstantiae, 2015. Online Publishing.