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Effect of preparation methods on phosphate removal of lanthanum-modified bentonite

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ABSTRACT

Excess phosphate in water can cause eutrophication, resulting in the destruction of water ecosystems. Phosphate removal has become one of the most important issues in wastewater treatment, and the adsorption is one of the important methods. Bentonite has been widely used for phosphate-containing wastewater treatment due to its low cost and large reserve. However, the unmodified bentonite usually has a relatively weak phosphate removal ability because of its negatively charge. Here, the lanthanum-modified bentonites were prepared by three methods (impregnation, acidification–impregnation, and ion exchange) in order to improve the phosphate removal capacity. The structures of the lanthanum-modified adsorbents were characterized and the effects of the modification method and adsorption conditions on the phosphate removal were investigated. The results show that the phosphate removal efficiency of the bentonite was increased after the lanthanum modification. In particular, the lanthanum-modified bentonite prepared by impregnating 0.1 mol·L^{-1} La^{3+} solution has the largest pore size and pore volume, which are 7.4 nm and 0.423 cm^3·g^{-1}, respectively. This lanthanum-modified bentonite also has the highest phosphate adsorption capacity, which is about 24.9 mg·g^{-1} at the optimal working conditions (initial phosphate concentration of 50 mg·L^{-1}, adsorbent dosage of 2 g·L^{-1}, temperature of 30°C, and pH of 6). The corresponding removal rate is as high as 99.5% in 30 min, while that of the raw bentonite is only about 26.8% in 60 min. The results show that the lanthanum-modified bentonite prepared by impregnation method could be a promising adsorbent for efficient phosphate removal.

Keywords: Bentonite; Lanthanum modification; Adsorbents; Impregnation method; Phosphate removal

1. Introduction

With the development of urbanization, more and more phosphorus-containing industrial effluent and municipal sewage have been discharged into various water bodies. Excess phosphate in water caused the eutrophication of water body that endangers water ecology and human health [1–3]. It is necessary to remove phosphate in wastewater before discharge. Various methods have been developed in recent years, including biological, physical, and chemical methods [4]. Both biological and chemical methods are highly susceptible to environmental influences and can even cause secondary pollution [5–8]. They are mainly used for the wastewater with low phosphate concentrations. On the contrary, adsorption is currently one of the more widely used physical methods for phosphate removal of industrial effluent [9]. Adsorbents with high specific surface area and porosity are usually used for phosphate adsorption.

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This method has many advantages, such as simple, stable, high adsorption capacity, easy operation, and no secondary pollution [10].

In order to meet the phosphate emission requirement of the treated wastewater with relatively low treatment cost, many adsorbents have been used. Those materials usually need to be sufficient, inexpensive, non-toxic and have strong phosphate adsorbing capacity, such as zeolite, activated carbon, fly ash [11–13]. Actually, natural adsorbents also have some problems, and should be modified before use [12]. In addition, nanocomposites, weak alkali fiber anion exchangers, new fiber ligand exchanges, polymer anion exchangers, and zirconium(IV) loaded fiber are very effective for phosphate adsorption with high selectivity and reusability but relatively high cost [14–17]. Bentonite as one abundant natural mineral, has strong ion exchange capacity and good adsorption property due to its large surface area and porosity [18]. However, the silicon-oxygen structure of bentonite leads to negative charge that reduces its phosphate absorbing capacity [19–21]. In order to enhance the adsorption property of bentonite, it is necessary to modify the bentonite by widening the interlayer spacing or increasing the cation exchange volume [22]. Lanthanum is an abundant and cheap rare earth element with a special electronic layer structure and is an electropositive element with a large atomic radius. These special structures give lanthanum strong chemical activity and good biocompatibility, and exhibits strong ligand adsorption to phosphate [20,23]. Kuroki et al. [24] used lanthanum to modify bentonite by ion exchange method. The adsorption data show that the adsorption could reach equilibrium in 60 min. When the initial phosphate concentration is 5 mg·L^{-1}, the phosphate removal rate could reach to 95% at room temperature. Yang et al. [25] prepared a modified biomass carbon by loading lanthanum ferrate nanoparticle whose saturation phosphate adsorption capacity is as high as 228.2 mg·g^{-1}.

In this work, lanthanum-modified bentonites were prepared by using three lanthanum-loading modification methods in order to enhance its phosphate removal performance. The structures of the bentonite before and after modifications were comparatively studied. The effect of the modification method and adsorption conditions on the phosphate removal in wastewater of the bentonites were investigated. The goal is to find an effective method to improve the phosphate removal performance of natural bentonite. This research may also inspire new avenues for bentonite modification to widen its use.

2. Materials and methods

2.1. Preparation of lanthanum-modified bentonite

Three methods were used to prepare the lanthanum-modified bentonites, as described below:

- Impregnation method: sodium bentonite (Na-B) (5 g) was added into 500 mL $LaCl_3$ solution (La^{3+} concentration: 0.4, 0.1, or 0.05 mol·L^{-1}) and stirred for about 24 h. After that, the mixture was centrifugated and washed with ethanol several times. The obtained bentonite was then subjected to three times of the above process to ensure adequate La^{3+} loading. The washed sample was dried in a vacuum oven at 80°C for 12 h. Finally, the modified bentonite was ground and sieved (200 mesh) for use. The obtained samples were labeled as La/B-I0.4, La/B-I0.1, and La/B-I0.05 according to the used La^{3+} concentration, respectively.
- Acidification–impregnation method: Na-B was firstly immersed in 20% sulfuric acid solution for 24 h, whose mass ratio was chosen as 1:10 according to the optimal condition. After that, the mixture was dried in a vacuum oven at 105°C for 24 h. Then, the acid-modified bentonite was immersed in a La^{3+} solution (0.3 mol·L^{-1}) for 24 h at room temperature. The ratio of bentonite mass to solution volume was kept as 1 g:50 mL and the pH value was adjusted to 10 with 0.1 M NaOH solution. After centrifugation and wash with ethanol several times, the mixture was dried in a vacuum oven at 80°C for 24 h. Finally, the obtained mixture was ground and sieved (200 mesh) for use and labeled as La/B-A.
- Ion exchange method: Na-B and Na_2CO_3 were firstly mixed in a beaker with appropriate deionized water for 1 h, and the mass ratio of Na-B and Na_2CO_3 is 10:3. The mixture was then transferred to a closed container and kept for 30 d to obtain high sodium-containing bentonite. After that, the mixture was filtrated and dried in a vacuum oven at 105°C for 24 h. Then, the obtained mixture was ground and sieved (200 mesh). Furthermore, the obtained bentonite (10 g) was gradually added to a La^{3+} solution (0.14 mol·L^{-1}) and stirred for 4 h to exchange Na^+ with La^{3+}. The mixture was centrifugated, washed with ethanol several times, and then dried in a vacuum oven for 24 h at 105°C. Finally, the obtained mixture was further ground and sieved (200 mesh) for use and labeled as La/B-E.

2.2. Characterization

The crystal structures of the samples were characterized by X-ray powder diffractometer (XRD, Rigaku D/Max-2400, Japan). The surface morphologies of the samples were analyzed by scanning electron microscopy (SEM, Hitachi S-4700). The specific surface area and pore size of the samples were characterized according to the N_2 adsorption–desorption isotherms conducted at –196°C (Nitrogen Adsorption Instrument, JW-BK100, China). The specific surface area (SSA) and pore-size distribution were calculated using the Brunauer–Emmett–Teller method, Barrett–Joyner–Halenda method, and density functional theory, respectively.

2.3. Phosphate adsorption

The simulated phosphate-containing wastewaters with different concentrations were prepared by using KH_2PO_4 as phosphorus source, and the pH value of the simulated wastewaters was adjusted with 0.1 M HCl or 0.1 M NaOH solutions. The detail procedure was as follows:

- 50 mL of the simulated wastewater with chosen pH value were taken for adsorption experiment;
- Adsorbent (2 g·L^{-1} or other dosages) was added into the taken wastewater and stirred at 200 rpm at the experiment temperature;

- During the adsorption process, about 2 mL of the mixture were taken out at certain time intervals (10–60 min);
- Filtrate was collected to measure the residual phosphate concentration by using a water quality tester (Lianhua Technology Co., Ltd., China);
- Phosphate removal efficiency was calculated by using Eq. (1).

$$\text{Removal efficiency}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where C_0 (mg·L^{-1}) is the initial phosphate concentration and C_t (mg·L^{-1}) is the phosphate concentration of wastewater treated after t min.

3. Results and discussion

3.1. Characterization of samples

The XRD patterns of the samples are shown in Fig. 1a. The characteristic diffraction peaks of the raw bentonite Na-B locate at 2θ of 6.5°, 10.4°, 17.3°, 20.7°, 25.3°, 26.6°, 27.2°, 29.1°, 31.3°, 35.1°, 39.7°, 45.4°, 48.5°, 62.2° and 68.2° [27,28]. It can be seen that the diffraction peaks of the three modified bentonites have some changes, which may originate from the ion exchange and La^{3+} loading. Here, the essence of the bentonite modification is the La^{3+} intercalation and exchange with other ions. La/B-I0.1 was obtained by adding Na-B to LaCl$_3$ solution to replace the interlayer ions with La^{3+} directly. For La/B-A, soaking the bentonite in sulphuric acid may dissolve the intercalated cations by H$^+$ exchange. The H$^+$ enters into the interlayers and replace the original Na$^+$, Ca^{2+} and Al^{3+}, which will weaken the interlayer force of the bentonite sample. This bentonite structure may be more favorable for the following La^{3+} exchange in the subsequent impregnation process. As Na$^+$ has a stronger exchange capacity than Ca^{2+} and Al^{3+} ions, La/B-E was obtained by firstly immersing the bentonite in Na$_2$CO$_3$ solution to increase intercalated Na$^+$ content [2]. The diffraction peak of Na-B at about 6.5° has moved towards a low angle after La^{3+} loading. It indicates that the layer spacing of the bentonite crystalline surface (001) increases due to the La^{3+} intercalation into the interlayer of montmorillonite. Besides, the intensity of some diffraction peaks of the bentonite after La^{3+} loading is significantly weakened, such as the peaks at about 29.1°, 31.3°, 35.1°, and 39.7°. It may be due to the fact that the modification process has weakened the interlayer bonding energy of bentonite. Furthermore, some impurities may be washed away, which results in the destruction of the interlayer crystalline structure of bentonite [29,30]. In addition, the tramp peaks of the three modified bentonites are reduced compared to Na-B, indicating that the modification process removed some of the impurities and the bentonite is purified.

The N$_2$ adsorption–desorption isotherms of the bentonite samples and correspondingly calculated SSA and pore structure parameters are shown in Fig. 1b and c. As shown in Fig. 1b, the amounts of N$_2$ adsorbed increase with

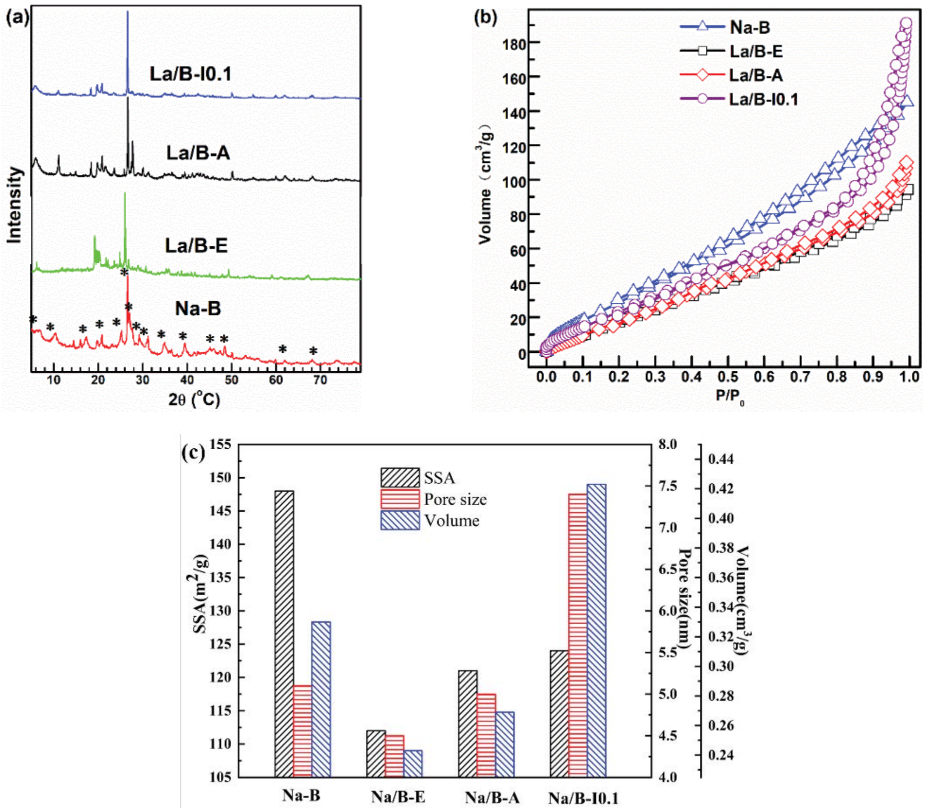

Fig. 1. (a) X-ray powder diffraction patterns of the samples, (b) N$_2$ adsorption–desorption isotherms of samples, and (c) pore structure parameters.

increasing the partial pressure. The curves of all the samples belong to type III according to the adsorption–desorption isotherm curve classification of International Union of Pure and Applied Chemistry (IUPAC). The isotherms of all the samples just show very weak lifts at the ultralow pressure part, which show the small amount of the micropore structure. The adsorption capacities of those samples increase at high relative pressure and the hysteresis loops also exist. Those phenomena show the existence of the mesopore structure in the sample, which are more obvious for La/B-I0.1. It can also be seen from Fig. 1c that the SSAs of all modified samples decrease compared to that of Na-B. The pore sizes and pore volumes of La/B-A and La/B-E also decrease, while those values of La/B-I0.1 increase on the contrary. Although the SSA of La/B-I0.1 decreases from 148 to 124 $m^2 \cdot g^{-1}$, the pore volume increases from 0.330 to 0.423 $cm^3 \cdot g^{-1}$, and the average pore size also increases from 5.1 to 7.4 nm. Above data shows that the pore in those samples are mainly mesopores and the impregnation method may be favorable for the formation of mesoporous structure. The increase in the mesopores content and their size may effectively improve the adsorption capacity of the adsorbent [31,32].

The SEM images of different bentonite samples are shown in Fig. 2. There are some obvious holes and cracks in Na-B, with a rough surface and some small particles (Fig. 2a). The surface structure of La/B-E in Fig. 2b has no obvious change compared with that of Na-B, but the number of small particles decreases and the surface roughness reduces. For La/B-A as shown in Fig. 2c, the surface is rougher with much more particles. But the cracks become less. Moreover, the holes in La/B-A are larger and deeper than that of Na-B. Sulfuric acid plays a role in "dissolving" and "washing" the ions intercalated in the bentonite layers during the acid modification, so the microstructure of the bentonite will undergo a certain change [33]. As shown in Fig. 2d–f, the number of cracks and pores in La/B-I0.1 reduces. But, a large number of particles with different sizes appear that may contribute to the increase in pore volume and the improvement of phosphate adsorption performance [34].

3.2. Phosphate removal performance of different bentonites

3.2.1. Effect of modification method

Fig. 3 shows the phosphate removal rates of different bentonite samples. The adsorption rates of all samples are relatively fast in the first 10 min. The reason is that the fresh bentonites have many unoccupied adsorption sites

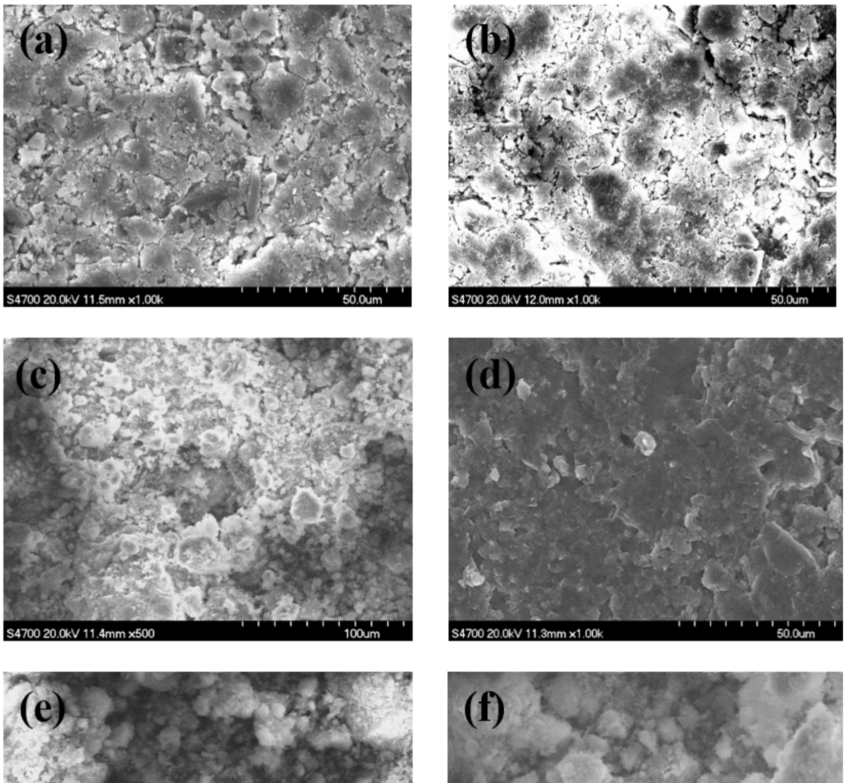

Fig. 2. Scanning electron microscopy images of (a) Na-B, (b) La/B-E, (c) La/B-A, and (d–f) La/B-I0.1.

on the surface and in the interlayer [35]. After 30 min, the adsorption capacities of the samples are approaching the saturation values except that of La/B-E. By comparison, it can be seen that the phosphate removal rates of Na-B and La/B-A are relatively much lower than that of other adsorbents. The corresponding values of the two samples are only 26.8% and 29.2%, respectively. The above results show that the acidification–impregnation method has only a weak positive effect on the phosphate removal ability of the bentonite. When the absorbing time exceed to 75 min, the phosphate removal rates of the above two samples even decrease to 21.7% and 24.9%, respectively. The acid modification may affect the structural stability of the bentonite. As result, the structure will further change during the adsorption–desorption process that led to the loss of some adsorption sites [36]. The phosphate adsorption capacity and corresponding removal rate of La/B-E are just about 13.6 mg·g^{-1} and 54.5% in 60 min, respectively. But, the absorbing capacity of La/B-E is gradually increasing with extending the treatment time even to 70 min, which is different from the adsorption isotherms of other samples. It is possible that La/B-E has the smallest SSA, pore volume and pore size among the samples although the La ion has been effectively loaded. So, it is inevitably that the relatively few and narrow diffusion channels will limit the ion diffusion although the absorption sites are adequate. The phosphate adsorption capacities of the bentonite samples modified by the impregnation method are obviously higher than that of the raw and modified bentonites, especially for La/B-I0.1. The phosphate removal rate in 10 min for La/B-I0.1 has reached to about 93.1%. Furthermore, the adsorption capacity of La/B-I0.1 achieves 24.9 mg·g^{-1} in 60 min, whose corresponding removal rate is about 99.5%. The results indicate that the impregnation is the best method to improve the phosphate removal capacity of the natural bentonite among the three methods. Phosphate removal for lanthanum-contained absorbent mainly originates from the reaction of La^{3+} with PO$_4^{3-}$ and the formation of complex lanthanum(III) phosphate [37]. The strongest phosphate removal performance of La/B-I0.1 may contribute to the effective La^{3+} loading, high pore volume and large pore size.

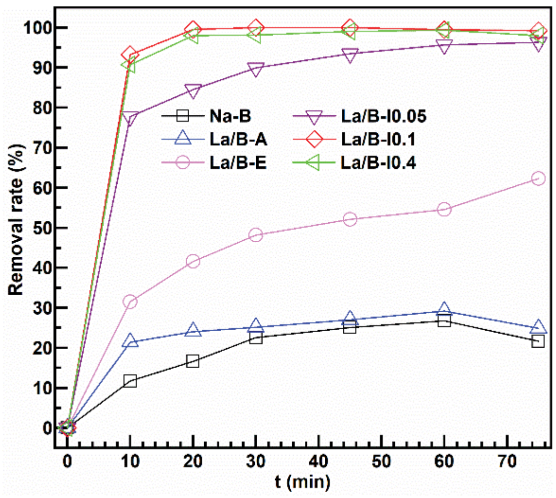

Fig. 3. Phosphate removal rate of different bentonite samples.

To further understand the adsorption of phosphate by these bentonite adsorbents, their adsorption kinetics were investigated by using the quasi-first-order equation and quasi-second-order equation models. The corresponding equations are as follows:

$$\text{Quasi-first-order model}: \ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{2}$$

$$\text{Quasi-second-order model}: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{3}$$

where q_e and q_t are the amounts of phosphate adsorbed (mg·g^{-1}) at equilibrium and at a certain adsorption time, respectively; t is the adsorption time (min). k_1 (min^{-1}) and k_2 (g·mg^{-1}·min^{-1}) are the quasi-first-order and quasi-second-orders rate constants, respectively.

The results are shown in Fig. 4 and Table 1. It can be found that the phosphate adsorptions of those adsorbents obey the pseudo-second-order kinetics. The R^2 value of La/B-I0.1 is above 0.99, which indicates the chemisorption

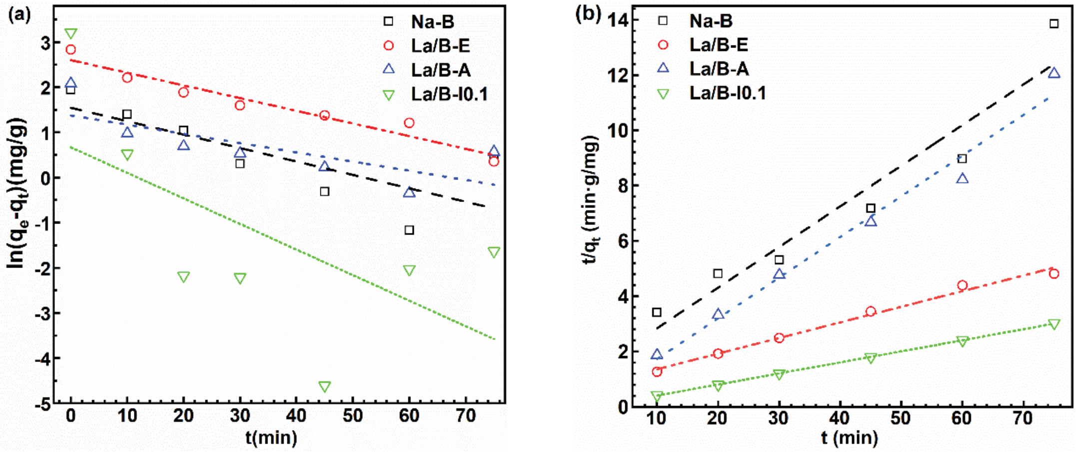

Fig. 4. Adsorption kinetics fitting parameters by lanthanum-modified bentonite (a) pseudo-first-order and (b) pseudo-second-order.

characteristic [38]. The equilibrium adsorption capacity is 25.0 mg·g^{-1}, which is consistent with the actual maximum adsorption capacity (24.9 mg·g^{-1}). Based on above results, La/B-I0.1 was chosen as the adsorbent for the following phosphate adsorption studies.

3.2.2. Effect of phosphate concentration and adsorbent dosage

The effect of initial phosphate concentration on the adsorption performance of La/B-I0.1 was investigated, and the concentration was adjusted in the range of 25–100 mg·L^{-1}. The corresponding phosphate removal rates are shown in Fig. 5a. It can be seen that the phosphate could be quickly removed by La/B-I0.1 when the phosphate concentration is no more than 50 mg·L^{-1}. When the initial phosphate concentration is about 25 mg·L^{-1}, the removal rate could reach about 100% in just 20 min. For 50 mg·L^{-1} of the initial phosphate concentration, the removal rate also approaches 99.5% in 30 min. At relatively low phosphate concentration, the bentonite adsorption capacity may be far from saturation, and still have many adsorption sites. When the initial phosphate concentration is as high as 75 or 100 mg·L^{-1}, the corresponding removal rates are just only about 73.3% and 58.8% in 60 min, respectively. The adsorption capacities of La/B-I0.1 are about 27.5 and 29.4 mg·g^{-1}, respectively. Both values are a little higher than equilibrium adsorption capacity (25.0 mg·g^{-1}). It indicates that high phosphate concentration promotes positive adsorption reactions and more adsorption sites are occupied, thus showing an increasing trend in the adsorption capacity of La/B-I0.1 [39]. The results also tell that La/B-I0.1 is suitable to treat the wastewater with phosphate concentration no more than 50 mg·L^{-1}. Fig. 5b shows the effect of the adsorbent dosage on the phosphate removal rate of La/B-I0.1. The dosage of adsorbent ranges from 1.0 to 4.0 g·L^{-1}. It can be seen that at a low dosage of La/B-I0.1 (less than 2 g·L^{-1}), the phosphate could not be complete removed. When the dosage of La/B-I0.1 is as high as 3 or 4 g·L^{-1}, the adsorption capacity decreases to 16.7 and 12.5 mg·g^{-1}, respectively. Therefore, in view of practicality and economy, the dosage of 2 g·L^{-1} is enough to treat the phosphate-containing wastewater with concentration no more than 50 mg·L^{-1}. For the following research, 50 mg·L^{-1} of the initial phosphate concentration and 2 g·L^{-1} of the adsorbent dosage were chosen.

3.2.3. Effect of adsorption temperature and pH value of wastewater

Fig. 6 shows the phosphate removal rates of La/B-I0.1 at different temperatures and pH values. It can be seen in Fig. 6a that the removal rate firstly increases with increasing the temperature from 15°C to 30°C, and then decreases with further increasing the temperature. The phosphate removal rate of La/B-I0.1 is close to 100% at 30°C while it

Table 1
Adsorption kinetics fitting parameters by lanthanum-modified bentonite

Sample	Capacity		Pseudo-first-order		Pseudo-second-order		
	Q (mg·g^{-1})	R^2	k_1 (min^{-1})	q_e (mg·g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2	q_e (mg·g^{-1})
Na-B	7.1	0.5867	0.0297	7.3	0.01572	0.9287	6.8
La/B-E	17.1	0.9396	0.0281	15.1	0.00041	0.9884	17.7
La/B-A	8.1	0.5529	0.0204	5.4	0.08260	0.9794	6.8
La/B-I0.1	24.9	0.3843	0.0566	43.8	0.14107	0.9999	25.0

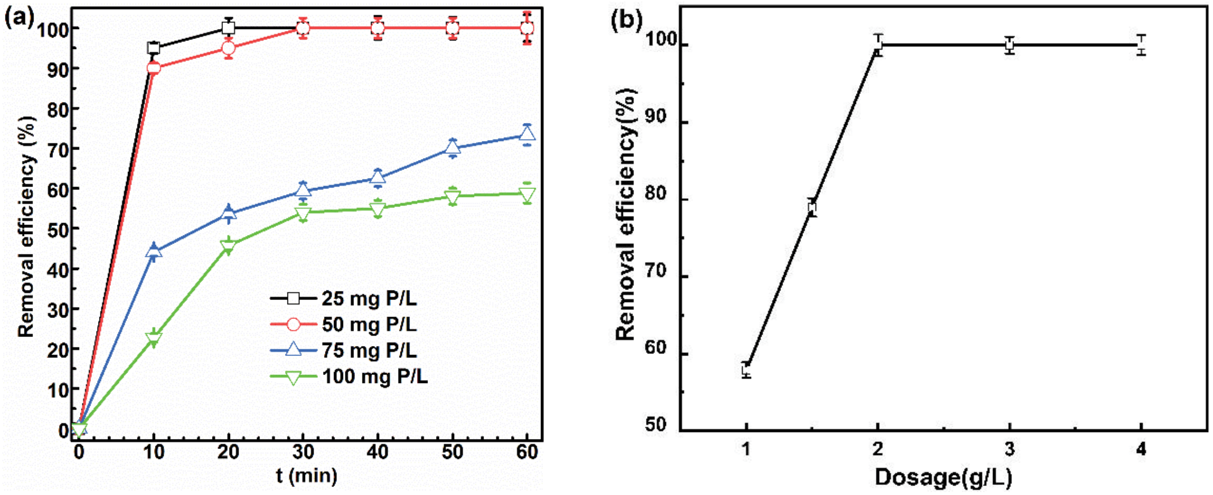

Fig. 5. (a) Phosphate removal rates of La/B-I0.1 at different initial phosphate concentration and (b) phosphate removal rates of La/B-I0.1 at different adsorbent dosage.

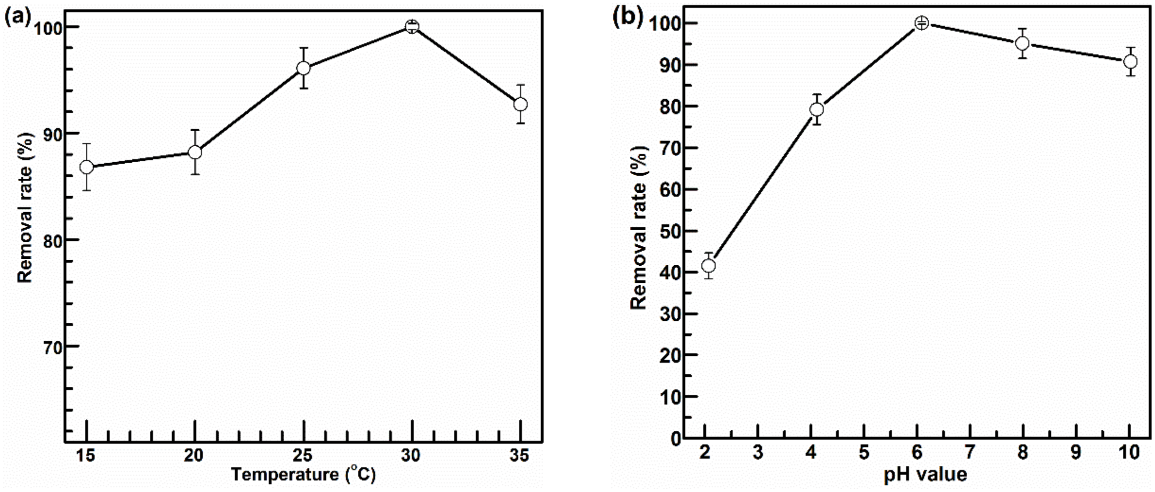

Fig. 6. (a) Phosphate removal rates of La/B-I0.1 at different temperatures and (b) phosphate removal rates of La/B-I0.1at at different pH values.

Table 2
Relevant parameters of adsorption isotherm model

Samples	Langmuir			Freundlich		
	q_m (mg·g^{-1})	R^2	k_L (L·mg^{-1})	k_F (mg·g^{-1})	1/n	R^2
La/B-I0.1	36.9	0.9539	0.0283	4.3836	0.3841	0.8461

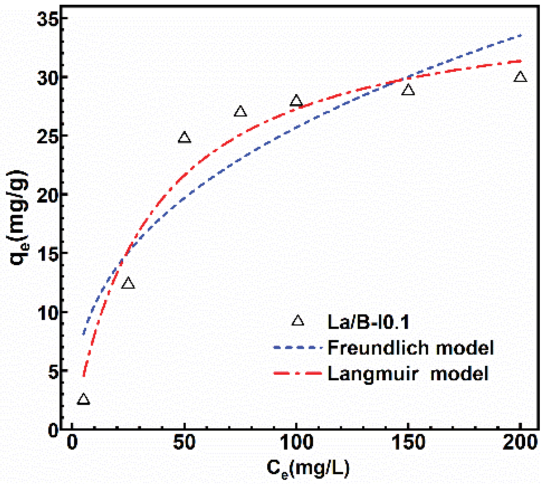

Fig. 7. Isothermal adsorption curve the La/B-I0.1.

reaches about 96.1% at 25°C. Raising temperature will be beneficial for improving the diffusion ability and rate of PO_4^{3-}, and thus phosphate could be adsorbed with relatively high speed [40]. However, the adsorption is an exothermic process and too high temperature may exacerbate desorption. Fig. 6b shows that the phosphate removal rate of La/B-I0.1 increases with increasing the pH value from 2 to 6. With further increasing the pH value in the range of 6 to 12, the removal rate gradually decreases. At acidic condition, the phosphate ion mainly exists as $H_2PO_4^-$, which has a better affinity with La^{3+}. On the contrary, the competitive reactions of OH^- and PO_4^{3-} with La^{3+} ion will happen under alkaline condition. As result, the formation of $La(OH)_3$ leads to the ineffective consumption of La^{3+}. Therefore, the optimal pH value for phosphate removal is 6 [41].

3.2.4. Phosphate adsorption mechanism of lanthanum-modified bentonite

The adsorption isotherm describes the equilibrium distribution of phosphate ions between the liquid and solid phases (adsorbent) under the given conditions. Establishing a suitable isothermal model is of great significance for predicting the adsorption efficiency and determining the adsorption mechanism. In order to study the adsorption mechanism of adsorbent to phosphate, two isothermal models are used for fitting [42–44]. The initial phosphate concentrations are chosen as 5, 25, 50, 75, 100, 150 and 200 mg·L^{-1}. The adsorption isotherm curves and corresponding fitting curves are shown in Fig. 7, and the relevant parameters are listed in Table 2. The experimental data has a higher correlation with the Langmuir model, where the R^2 is 0.9539. It indicates that the surface structure of the La/B-I0.1 is relatively homogeneous and the phosphate adsorption on this adsorbent is mainly a monolayer chemisorption process [37]. According to the fitted result, the theoretical maximum saturated adsorption capacity is 36.9 mg·g^{-1}. The results show the strong phosphate adsorption ability of La/B-I0.1.

4. Conclusions

In this study, the bentonite was modified by three different methods to get lanthanum-containing adsorbents for phosphate removal in wastewater (impregnation, acidification–impregnation, and ion exchange methods). The N_2 adsorption–desorption curves, XRD as well as SEM data confirm that the bentonite prepared by impregnating with 0.1 M of La^{3+} solution has the largest pore volume and size among those modified bentonites (0.423 $cm^3 \cdot g^{-1}$ and 7.4 nm, respectively). The La loading modification could increase the phosphate removal rate of the bentonite, especially for the samples modified by the impregnation method. The bentonite prepared by impregnating with 0.1 M of La^{3+} solution has the highest phosphate absorbing capacity among the bentonite samples. At the optimal working condition (50 $mg \cdot L^{-1}$ of initial phosphate concentration, 2 $g \cdot L^{-1}$ of adsorbent dosage, 6 of pH value and 30°C of temperature), the maximum adsorption capacity of this absorbent is up to 24.9 $mg \cdot g^{-1}$. The above value is approximately four times higher than that of the raw bentonite. The results show the La-loading bentonite prepared by the impregnation method could become a promising and suitable material for the phosphate removal in wastewater.

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