



Phosphate removal from wastewater by model-La(III) zeolite adsorbents

NING Ping^{1,*}, BART Hans-Jörg², LI Bing³, LU Xiwu³, ZHANG Yong¹

1. Department of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China.

E-mail: ningping58@sina.com

2. Lehrstuhl für Thermische Verfahrenstechnik, TU Kaiserslautern, D-67653 Kaiserslautern, Germany

3. Department of Environmental Engineering, Southeast University, Nanjing 210096, China

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Abstract

Phosphorus is one of the primary nutrients which leads to eutrophication and accelerates aging process in enclosed water bodies. Because of the poor phosphorus selectivity of other adsorbents, the novel La(III)-modified zeolite adsorbent (LZA) was prepared by modifying 90 nm zeolite with lanthanide to selectively remove phosphate in the presence of various omnipresent anions, such as sulfates, bicarbonates, and chlorides. Through batch and fixed bed operation, the following optimum conditions were obtained: concentration of lanthanum chloride solution 0.05 mol/L; solid/liquor ratio 1/25; pH 10; calcination temperature 550°C; time 1 h. The value of the Freundlich model constants K_f and $1/n$ were found to be 16.76 mg/L and 0.2209, respectively. In addition, when calculated at pH 6.0, distribution coefficient K_D could be as high as 36.6. Furthermore, in the alkaline pH range, solution of 0.8 mol/L NaCl was used to regenerate the saturated LZA, which could reach the high regeneration efficiency as high as 100%. Because of the good selectivity and regenerability of LZA, it might serve as a potential way for advanced phosphate removal from the sewage containing other anions.

Key words: phosphate; adsorption; zeolite; regeneration; distribution coefficient

Introduction

It was indicated in the Environmental Report in China (Xia, 2005) that almost all the rivers and lakes were more or less contaminated. Groundwater in most cities was also polluted by human activities, and has been increasingly deteriorated. Water pollution, especially, eutrophication caused by phosphorus and ammonia, is still a problem the society will also face in the future. The presence of trace level phosphate (even less than one part per million) in the treated wastewater from municipalities and industries is often responsible for eutrophication, which has led to short and long term environmental problems in lakes, coastal areas, and other confined water bodies (Zhao, 1997). Many technologies have been applied and examined to remove phosphorus from wastewater due to the increasingly stringent regulations on phosphorus discharge (Zhu and Jyo, 2005). Chemical precipitation (CP) and biological nutrient removal (BNR) are the two most common methods for phosphate removal from wastewater (Oguz *et al.*, 2003; Strickland, 1998; Wade *et al.*, 2004; Alexandratos, 2007). Essentially, these processes transfer phosphate from the liquid phase to the sludge phase, which needs to be subsequently transported and disposed of elsewhere. Also, complete removal was unattainable by CP and BNR due to thermodynamic and kinetic limitations. Thus, extensive research has been carried out in the world

to find out selective sorbents for phosphate removal accompanied with operational simplicity and adaptability to different wastewater composition, flow rate, and temperature (Urano and Tachikawa, 1991; Cengeloglu *et al.*, 1998; Balaji and Matsunaga, 2002). Zhao and Sengupta (1998) have summarized the critical disadvantages limiting the application of present sorbents, among which were poor selectivity toward phosphate over competing anions and other dissolved organics, low adsorption capacity in the neutral pH range, gradual loss of adsorption capacity due to fouling phenomena associated with other concomitants, and inefficient regeneration.

Zeolite was introduced into wastewater treatment because of its large specific surface area and selective adsorption, such as ammonia, dissolved organic matter, and some other cations. The research on the ion exchange and sorption capacity of different modified zeolites has been widely reported (Tokunaga *et al.*, 1997; Chen *et al.*, 2006). Murayama discussed how the zeolite, synthesized from fly ash of coal, could simultaneously adsorb ammonia and phosphate (Murayama *et al.*, 2003). Tokunaga *et al.* (1997) directly used lanthanum compounds to remove As(V) ion from aqueous solution, and obtained high removal efficiency in a proper pH range. At optimum pH value of 6.5, adsorption of fluoride onto mixed rare earth oxides presented a promising efficiency. Among the cases above, however, there was a problem in terms of both efficiency and costs. New techniques should be developed

* Corresponding author. E-mail: ningping58@sina.com.

to reduce concentration of phosphorus pollutants to an environmentally acceptable level with affordable costs. Because of the sharp reduction of available phosphorus resource, phosphate removal and recovery from wastewater should both be considered during the process of waste water treatment. Unfortunately, few studies have been carried out on this aspect. Furthermore, the mechanism of cation removal by the modified zeolite has not adequately been clarified yet.

In this study, a novel La(III)-modified zeolite adsorbent (LZA) (Li *et al.*, 2005) was recently developed at Southeast University, Jiangsu Province, China, to selectively remove phosphate from compound solutions. Along with the adsorption kinetics, the influence of pH, adsorbent quantity, and presence of competing anions, such as its sulfate and bicarbonate, on adsorption efficiency of phosphate have been investigated.

The objectives of this study were to (1) probe the equilibrium adsorption capacity of LZA for phosphate in the presence of high concentration of competing anions; (2) test phosphate breakthrough behaviors in a multicomponent system; (3) determine the effect of pH; (4) identify characteristics and adsorption isotherms of the new adsorbents; (5) find out the regenerability of the saturated LZA and reusability of spent regenerant brine.

1 Experiment

1.1 Raw material

As raw material of LZA, natural zeolite was obtained from Weichang County, Hebei Province, China. It was slightly gray with a high density and low hardness. XRD analysis indicated that its composition was mainly clinoptilolite, whose concomitant materials were little granite, quartz, and red stone. The chemical components of natural zeolite and LZA are listed in Table 1.

1.2 Preparation of adsorbent

First, the natural zeolite was broken into small fragments, which then was ground and screened into zeolite particles with diameter of 90 nm. Second, the zeolite powder was put into La₂O₃ solution for modification treatment. After filtration and cleanness, the modified zeolite was calcined at certain temperature for dehydration and to get rid of the impurities. Finally, the LZA was sealed and reserved for further experiments. The chemical components and physiochemical property of LZA are presented in Tables

1 and 2, respectively.

1.3 Apparatus

All the reagents were of analytical grade level. 721 spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., China), Sartorius PB 220 pH meter (Sartorius, Germany), Leica stereoscan 420 scanning electron microscope (SEM) (Leica, Germany), and XRD-600 (Shimadzu Corporation, Japan) were used for chemical analysis. Samples were kept air tightness to prevent hydration. The surface of the modified zeolite was observed with SEM. In addition, TG-328B electro optic analytical balance (Hangzhou Gaoxin Electronic Co. Ltd., China), MP1100B electronic balance (Shanghai Hengping instrument Co. Ltd., China), HY-2 multiuse electronic oscillator (Jiangyan Xinkang Medical Apparatus Co. Ltd., China), DZKW-4 electronic thermo stable water boiler (Jinan Meifeng, China), and SRJX-4-15 box-type furnace (Shanghai Hongtong, China) were used in this study.

1.4 Experimental procedure

The solution of phosphate was prepared by dissolving reagents of analytical grade solid samples in deionized water. Then, the solution was further diluted to a suitable concentration, and the optimum pH was adjusted by adding solution of 0.1 mol/L HCl or NaOH. All the tests were conducted thrice to obtain reproducible results with an error of less than 5%.

2 Results and discussion

2.1 Characteristics of adsorbent

Considering the economical and technological feasibility, the optimum conditions of modification are presented as follows: the concentration of lanthanum chloride solution was 0.05 mol/L and the appropriate solid/liquor ratio was 1:25 at pH 10 (Li *et al.*, 2005). Fig.1 shows the SEMs of natural zeolite and modified zeolite. It was clear from Fig.1a that the natural zeolite possessed an orderly and even Si-O structure with few impurities on its surface. In Fig.1b, the well dispersed white materials were lanthanum oxides that were produced from thermal decomposition after calcination at 600°C. As an active component in LZA, La₂O₃ played an important role in the process of adsorption.

By comparing Figs.1a and 1b, distinct differences existed between the two images. After modification of zeolite

Table 1 Chemical component of natural zeolite and LZA

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	La ₂ O ₃
Natural zeolite	75.61	18.19	3.06	2.17	0.66	0.15	0
LZA	75.48	18.14	2.99	2.13	0.62	0.13	0.2

Table 2 Physiochemical properties of LZA

Parameter	ρ_p (g/ml)	δ (ml/g)	ε (cm ³ /g)	d (nm)	ζ (°C)	s (m ² /g)
Tested value	1.27	0.3	0.47	0.4	< 700	550-600

ρ_p : density of particle; δ : pore volume; ε : pore ratio; d : pore diameter; ζ : thermal stability; s : specific area.

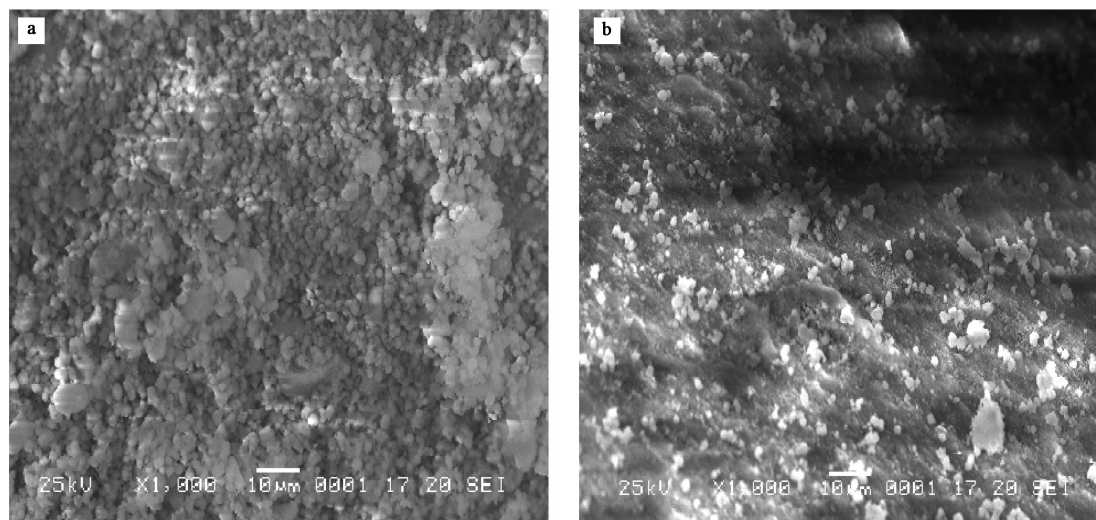


Fig. 1 SEMs of natural zeolite (a) and LZA (b).

through active lanthanum oxide, which enhanced the adsorption capacity of natural zeolite, the targeted negative ions could be removed effectively. The adsorbent was characterized in terms of specific area and pore diameter. The adsorbent had a mean pore diameter of 0.4 nm, the specific area was in the range of 550–600 m²/g. Other parameters are listed in Table 2.

2.2 Adsorption isotherms

Figure 2a shows the adsorption isotherm of phosphate onto natural zeolite and LZA. The adsorption capacity of LZA for phosphate was found to be 24.6 mg/g. The data correlated well with the linear form of Freundlich adsorption (Fig.2b) isotherm model, which were given by Eq.(1):

$$\log q_e = \log K_f + (1/n)\log C_e \quad (1)$$

where, C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity of P (mg/g), K_f (mg/L), and $1/n$ are the Freundlich constants. The value of the constants K_f and $1/n$ are found to be 16.76 mg/L and 0.2209 for LZA, respectively; whereas the value of the constants K_f and $1/n$ are found to be 0.45 mg/L and 1.5929 for natural zeolite, respectively. This shows that a multilayer of phosphate was formed on the surface of LZA, and that the adsorption capacity of LZA increased

dramatically because of the function of hydrate lanthanum loaded on the zeolite.

2.3 Influence of adsorbent quantity

Figure 3 shows the influence of LZA quantity on the adsorption capacity of phosphate under the condition of pH 6.2, phosphate concentration 1.5 mg/L, and contacting time more than 2 h. The final pH value was around 7. The adsorption capacity of phosphate increased with the increase of LZA quantity. Almost 99.5% phosphate was adsorbed on LZA when its quantity reached 0.8 g/L. Further, when the LZA reached 1.2 g/L, there was only a small adsorption capacity of phosphate. Therefore, LZA quantity of 0.8 g/L was used in further experiments. The initial or the final pH values were not affected by the LZA quantity.

The binding ability between an element and the surface was reflected by distribution coefficient K_D (m³/kg), which was related with pH and the type of surface. The distribution coefficient for phosphate and LZA at pH 6.0 was calculated by the following equation (Raichur and Basu, 2001):

$$K_D = \frac{C_s}{C_w} \quad (2)$$

where, C_s is the concentration of phosphate on the LZA

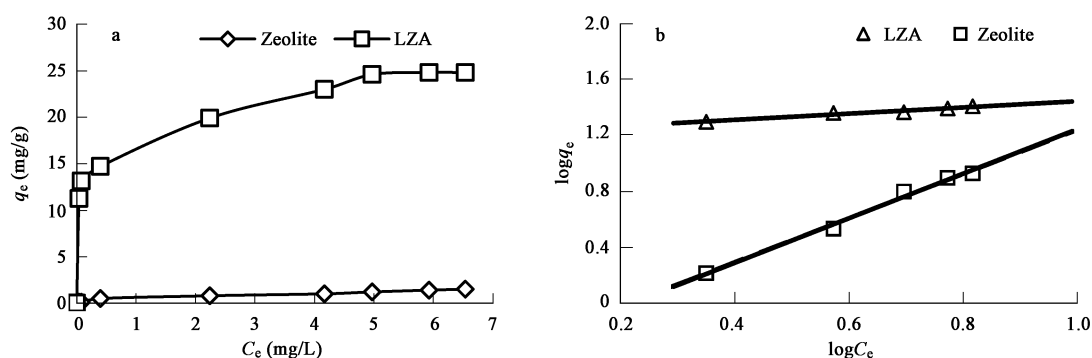


Fig. 2 Adsorption isotherms (a) and Freundlich model (b) under the condition of 20°C, pH 6.0, 1.5 mg/L phosphate concentration and 24 h contact time.

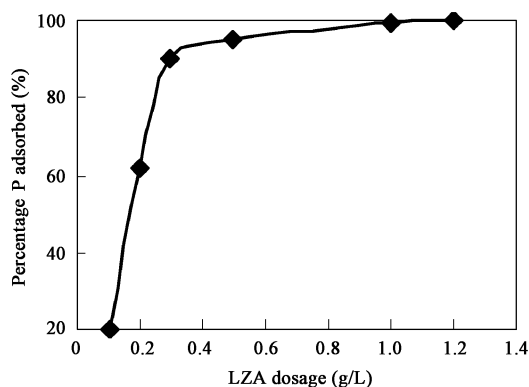


Fig. 3 Effect of adsorbent quantity on the adsorption capacity under the condition of pH 6.0, 1.5 mg/L initial phosphate concentration, and 2 h contact time.

surface (mg/kg), and C_w is the concentration in water solution (mg/m³). It is observed that K_D value increased with the increase of LZA quantity, in the test because of the value of K_D was as high as 36.6 m³/kg. This shows that the LZA has good selectivity for phosphate removal from solution.

2.4 Effect of pH value

The pH value of solution played a major role on the adsorption capacity of phosphate. The adsorption might be probably favored by low pH value because of anion adsorption coupling with the release of hydroxyl anions. Adsorption was studied in the pH range of 2–9 (Fig.4). It indicated that adsorption capacity was maximum in the pH range of 4–6. In the strongly acidic pH range, the adsorption capacity of phosphate slightly decreased, this could be attributed to the formation of a weak hydrophosphorus salt or polymeric P-LZA (Fig.4). In the alkaline pH range, there was a sharp drop in adsorption capacity, which might be due to the competition of hydroxyl ion with phosphate for adsorption on LZA. The mechanism could be explained in Fig.5. The process of oxide hydration was able to adsorb anion groups because of their positive site.

On the basis of the experimental results and analysis, the lanthanum oxide loaded on the zeolite served as the functional group to adsorb targeted anions. Therefore, the mechanism of the reaction could be attributed to the adsorption among the oxides and oxyacids.

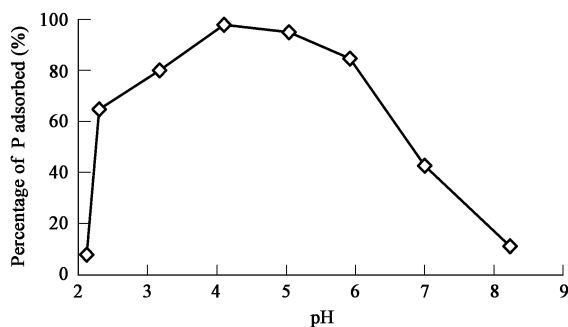


Fig. 4 Effect of equilibrium pH on adsorption capacity under the condition of 1.5 mg/L phosphate concentration, 1 g/L LZA quantity, and 3.5 h retention time.

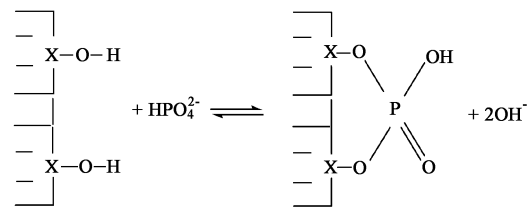


Fig. 5 Hypothesis of phosphate removal by LZA adsorbent.

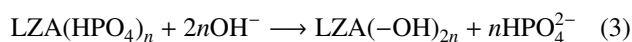
2.5 Selectivity

In real systems, there are several other anions, such as sulfates, bicarbonates, and chlorides, which might compete for the sorption sites with phosphate. To assess the effects of these anions, the tests were conducted in the presence of 1.5 mg/L P, and 300 mg/L potassium sulfate, calcium bicarbonate, and sodium chloride concentrations, respectively. These experiments were carried out in minicolumns filled with 3.0 g LZA and a velocity of 6 m/h.

The adsorption superiority order of anions were in the following order: $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^-$ (Fig.6). Chloride, sulfate and bicarbonate concentrations increased quickly. In addition, the breakthrough was obtained when the effluent was even less than 800 bed volumes. However, LZA remained efficient for phosphate adsorption when the effluent was around 5,500 bed volumes. Competing anions in the effluent from sewage treatment plant did not affect the phosphate adsorption capacity by using LZA as adsorbent. Thus, LZA might be used for advanced phosphate removal in effluent from sewage treatment plants.

2.6 Regeneration

La(III)-modified zeolite adsorbent should be effectively regenerated so it could be used for multiple cycles of operations. The adsorption of phosphate involves electrostatic, Lewis acid-base, and hydrophobic interactions. The high pH is necessary to convert bidentate phosphate to its monodentate species, thus, reducing its sorption affinity. The regeneration of LZA could be regarded as the reverse reaction of its adsorption (Eq. (3)).



The saturated adsorbent was regenerated with the 0.8 mol/L NaCl solution at pH 10.5 in the fixed minicolumn bed. The regenerant flowed slowly through the fixed bed.

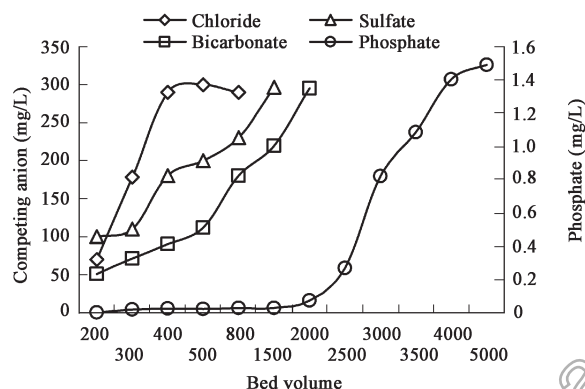


Fig. 6 Phosphate selectively adsorbed by LZA from competing anions.

More than 90% of adsorbed phosphate was recovered in the first cycle by using less than 10 bed volumes of regenerant, and nearly 100% recovery efficiency was achieved in the subsequent cycles. In the seven regeneration experiments, adsorption capacity of regenerated LZA was never lower than 90% of that of the fresh LZA (Fig.7), which meant that the adsorbent possessed a good regenerability.

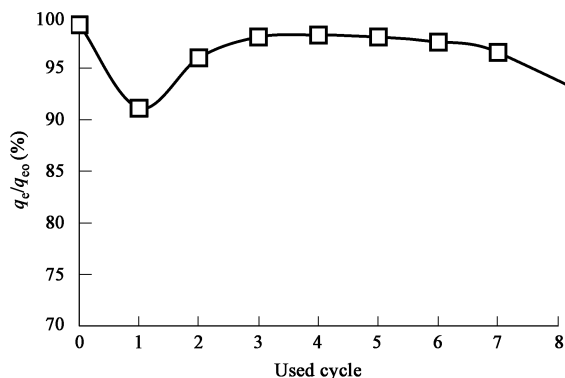


Fig. 7 Variation of adsorption capacity influenced by LZA used cycles.

3 Conclusions

The results of batch experiments and fixed bed operation showed that LZA might serve as a unique means for selective removal of phosphate in the effluent from the sewage treatment plant, which contained other anions, such as sulfates, bicarbonates, and chlorides.

Adsorption of phosphate onto LZA under the condition of 20°C, pH 6.0, 1.5 mg/L phosphate concentration and 24 h contact time, could be fitted well with Freundlich model. The calculated value of distribution coefficient (K_D) between solution phase and LZA at pH 6.0 increased with the increase of adsorbent quantity. The value of K_D was as high as 36.6 m³/kg, which meant the LZA possessed a good selectivity for phosphate removal in the effluent from the sewage treatment plant.

In the seven regeneration experiments, adsorption capacity of regenerated LZA was never lower than 90% of that of the fresh LZA, which meant a good regenerability of LZA.

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