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The feasibility of adopting zeolite in phosphorus removal from aqueous solutions

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ABSTRACT

Excess phosphorus in waterways can cause serious eutrophication, a phenomenon which could eventually result in water quality crisis. Thus, there is a need to seek appropriate ways to remove phosphorus from wastewater. This investigation evaluates the potential of two types of sorbents, granular zeolite (A) and globular zeolite (B), for phosphorus removal. The comparative adsorption of phosphorus from aqueous solutions by A and B is tested using batch experiments. For A and B, the assessed optimum pH is 1.8 and 2.0, sorbent dosage 2.5 and 30 g (per 100 ml aqueous solution, and the contact time intervals 20 and 40 min, respectively. The initial phosphorus concentration for both sorbents was 20 mg/L. The analysis of the results demonstrates that sorbent A has better adsorption characteristics than B. To describe the equilibrium adsorption isotherms, Langmuir and Freundlich models are applied to the data. The Langmuir isotherm adequately describes adsorption for both of these sorbents, with an R^2 goodness of fit of 0.9792 for A and 0.9835 for B, respectively.

Keywords: Phosphorus removal; Zeolite; Equilibrium isotherm

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1. Introduction

It is well known that phosphorus is a significant contributor to the growth of phytoplankton, which leads to serious eutrophication [1,2]. This phenomenon can commonly cause deterioration of water quality and eventually pose a human health risk [3]. Therefore, the topic of phosphorus removal has been of high importance for water and wastewater treatment [4].

Zeolites are naturally occurring hydrated aluminosilicate minerals of a porous structure; mainly consist of three-dimensional frameworks structure where the aluminum and silicon structure atoms are bound by covalent bounds over shared oxygen atoms to form interconnected cages and channels [5,6]. This structure results in valuable physicochemical properties such as ion-exchange, molecular sieve, catalysis, and adsorption capabilities. The utilization of zeolites for environmental applications is getting new research attention chiefly due to these properties, their low cost, and worldwide occurrence.

Adsorption is an attractive option for simple and effective water and wastewater treatment in comparison to the traditional chemical precipitation and biological processes [5,7,8]. There has been increasing interest in the utilization of zeolite for the removal of phosphorus in the last decade [9–13]. However, the

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authors have observed that previous research did not explicitly investigate the key influencing factors in phosphorus adsorption by zeolites. Additionally, each variety of zeolite has unique adsorption characteristics requiring individual examination. This work explores the potential application of zeolite as a kind of sorbent, investigating the efficiency of two sorbents, granular (A) and globular (B) zeolite, for the removal of phosphorus from synthetic aqueous solutions by batch experiments.

2. Materials and methods

2.1. Sorbent

This research investigates the use of zeolite media as a sorbent for removal of phosphorus. This includes both granular (A) and globular (B) zeolite. The effective sizes of the granular (A) sorbent ranged from 20 to 40 meshes and the globular shaped sorbent (B) from 1.0 to 2.0 mm. Zeolite A was provided by Sinopharm Chemical Reagent Co., Ltd (China) and B was obtained from Fine Chemistry Industry Organization of Guangfu, Tianjin (China). Table 1 gives the chemical composition of sorbent A and B. These two zeolites were applied without any preliminary treatment in these experiments.

2.2. Chemicals

Analytical quality chemicals were used for adsorption tests. All solutions were prepared with deionized water.

Aqueous solutions containing phosphorus at various concentrations were prepared by dissolving an accurately weighed sample of anhydrous potassium dihydrogen phosphate (KH_2PO_4) in deionized water. The initial pH adjustment was done by employing a suitable volume of 0.1 M sodium hydroxide or 0.1 M sulfuric acid.

Table 1
Chemical composition of sorbents A and B

Chemical composition (%)	Zeolites	
	A	B
SiO_2	58.80	71.54
Al_2O_3	18.31	13.64
Fe_2O_3	3.69	2.83
CaO	2.03	1.88
MgO	4.73	1.69
Na_2O	0.68	1.86
K_2O	1.15	4.06
TiO_2	0.12	0.32
LOI[a]	10.49	2.18

[a] Loss of ignition.

Measurements of the initial and final pH of the phosphorus ion solutions were accomplished using a laboratory pH-meter (pHS-3C, Shanghai Precision and Scientific Instrument Co., Ltd). A preliminary calibration was systematically performed by the use of suitable buffer solutions.

Total phosphorus concentration was determined by adopting the ascorbic acid method [14] at the wavelength of 700 nm using a 722 visible spectrophotometer (Shanghai Lengguang Instrument Co., Ltd.).

2.3. Phosphorus adsorption experiments

The phosphorus adsorption batch experiments involved testing the effect of pH, sorbent dosage, and initial phosphorus concentration on phosphorus adsorption, as well as kinetic studies and development of adsorption isotherms.

These experiments were performed as follows. The sorbents were equally distributed in Erlenmeyer flasks, after which were then filled with a solution containing a certain concentration of phosphorus. The flask was sealed and then placed in a thermostatic shaker bath for the required time. Subsequently, the mixture was centrifuged and then the supernatant phosphorus concentrations were examined using the ascorbic acid method [14].

In order to lower the experimental errors, all of these experiments were conducted in triplicate and the mean values were adopted.

2.4. Analytical methods

2.4.1. Equilibrium adsorption model

The removal efficiency (E, %) and the amount of adsorbed phosphorus (q_e, mg or µg of P per g zeolite) were calculated as follows:

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where C_0 is the concentration (mg/L), C_e is the final equilibrium concentration (mg/L), V is as the volume of the test solution (L), and m is the mass of added zeolite (g).

2.4.2. Adsorption isotherm model

Langmuir and Freundlich isotherms were developed to characterize phosphorus removal and adsorption capacity of the two zeolites. These two models are generally used to illustrate observed adsorption phenomena.

The Langmuir isotherm, for a single solute, is given by Eq. (3), whereby the parameter q^0 is defined as the monolayer capacity attained at high concentrations (mg/g) and b the equilibrium constant (L/mg) [15]. q_e and C_e are as defined in Eqs. (1) and (2).

$$q_e = \frac{b \times q^0 \times C_e}{1 + b \times C_e} \tag{3}$$

The Freundlich isotherm model is described in the following equation:

$$q_e = K \cdot C_e^{\frac{1}{n}} \tag{4}$$

where K is the measure of adsorption capacity, $\frac{1}{n}$ refers to adsorption intensity parameter, and other parameters have been defined above.

3. Results and discussion

3.1. Effect of initial pH

The influence of pH on the adsorption of phosphorus was assessed by contacting 2.5 g of sorbent A and 0.1 L of an aqueous solution of phosphorus. For sorbent B, 30 g of sorbent and 0.1 L phosphorus solution were mixed in the same manner. Experiments were undertaken at various initial pHs ranging between 1.8 and 12. An initial phosphorus concentration of 20 mg/L was applied, suspensions stirred for 20 min at a rate of 170 rpm, and subsequently centrifuged for 15 min. Finally the supernatant was measured by the use of the ascorbic acid method. This test was performed at room temperature (25℃).

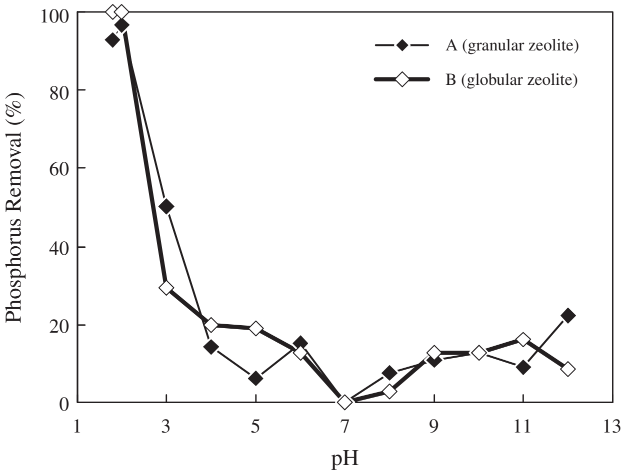

Fig. 1. Effect of pH on phosphorus adsorption by sorbents A and B.

Fig. 1 depicts phosphorus removal by the zeolites, for pH values ranging from 1.8 to 12. This shows the highest phosphorus removal efficiency—close to 100%—for sorbent A and B at a pH of 1.8 and 2.0, respectively. This removal efficiency declines rapidly for both sorbents to 0% at pH 7, with a slight increase with higher pH levels. Possible explanations for these results include: (1) in acidic conditions, zeolite pores are expanded due to reaction of components such as Al_2O_3 and Na_2O with acid, augmenting specific surface area (Table 2), and energy; and (2) in alkaline conditions, chemical precipitation covers the domain position in the course of adsorption.

Table 3 shows that pH values after adsorption increased for initial pH values lower than 9 for A and 11 for B. The adsorption of phosphorus onto mineral surface may be described by a ligand exchange mechanism [16], which causes an increase in pH due to the hydroxyl ions release from the sorbents.

3.2. Effect of dosage of zeolites

To estimate the relationship between phosphorus removal and sorbent dosage, adsorption experiments were carried out at pH 1.8 for A and pH 2.0 for B, in 0.1 L stirred (for 20 min) glass flasks containing

Table 2
The variation of specific surface area with pH in acidic conditions

Zeolites	Initial	Specific surface area (m^2/g)					
		pH					
		1.8	2	3	4	5	6
A	42.885	88.368	86.957	68.469	59.482	53.348	49.356
B	19.232	46.029	45.632	38.698	33.325	28.769	22.823

Note: BET Surface area meter, Builder, China.

Table 3
Comparison of pH values before and after adsorption

	pH												
Before		1.8	2	3	4	5	6	7	8	9	10	11	12
After	A	4.67	5.86	7.10	7.86	8.00	8.31	8.58	8.15	8.99	9.11	9.41	9.89
	B	5.20	6.76	8.95	10.33	10.48	10.59	10.62	10.68	10.63	10.76	10.65	10.68

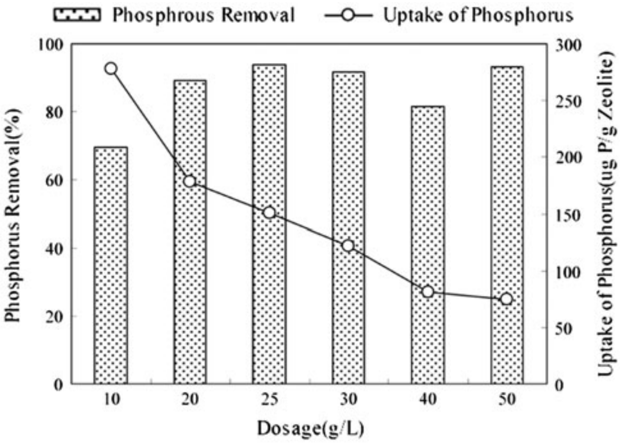

Fig. 2. Effect of sorbent dosage on phosphorus removal and uptake for A.

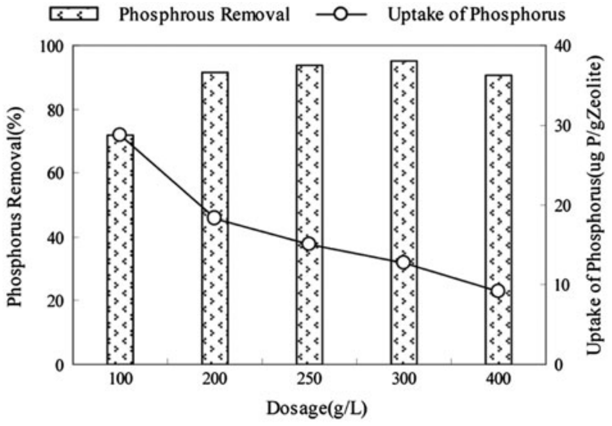

Fig. 3. Effect of sorbent dosage on phosphorus removal and uptake for B.

various masses of A or B and 0.1 L of phosphorus containing solutions. The suspensions were centrifuged (15 min) and the solutions were assessed for final phosphorus ion concentration.

The removal efficiency of phosphorus as a function of dosage for sorbents A and B is shown in Figs. 2 and 3. As expected, the results indicate an optimum zeolite dosage, corresponding with the maximum phosphorus removal efficiency (%); these are 25 g/L (93.9% removal) for sorbent A and 300 g/L (93.8% removal) for sorbent B.

The relationship between uptake and dosage appears in contrast to the trend of phosphorus removal for both sorbents. This indicates a decrease in adsorption capacity per unit mass of sorbent with the increase in sorbent dosage, potentially mitigating to some extent the trend observed in increasing removal efficiency with sorbent dosage. This loading mass declines with increasing dosage from 277.8 to 74.5 μg per g A, and 28.7 to 9.1 μg per g B, respectively. Reasons for this decrease might include the aggregation at higher solid/liquid ratios or precipitation of particles with increasing dosage.

This analysis of phosphorus removal and the uptake shows that A outperforms B in the course of adsorption and indicates an optimum dosage of 2.5 g/L for A and 30 g/L for B to be utilized for the following experiments.

3.3. Adsorption kinetic study

The kinetics of phosphorus adsorption was determined following the same experimental procedure described above but by varying the contact time. The optimum dosage and pH, as determined in previous experiments, were used for each sorbent.

Fig. 4 explores the relationship between phosphorus removal and reaction time during the course of adsorption for granular and globular zeolites. The phosphorus removal rate rises sharply for the first 20 min, at which it is close to maximum. The maximum phosphorus removal for sorbent A of 94.0% is reached at 20 min, and the maximum removal for sorbent B of 96.7% of B at 40 min. These maximum contact time intervals were used for the subsequent tests.

3.4. Effect of initial phosphorus concentration

Experiments to evaluate the influence of initial phosphorus concentration on phosphorus removal were conducted using the same conditions as for the previous experiments, but varying the initial phosphorus concentration.

Fig. 5 reveals phosphorus removal and phosphorus uptake at different initial phosphorus concentrations with application of zeolites A and B. The phosphorus loading behavior of zeolite used in this

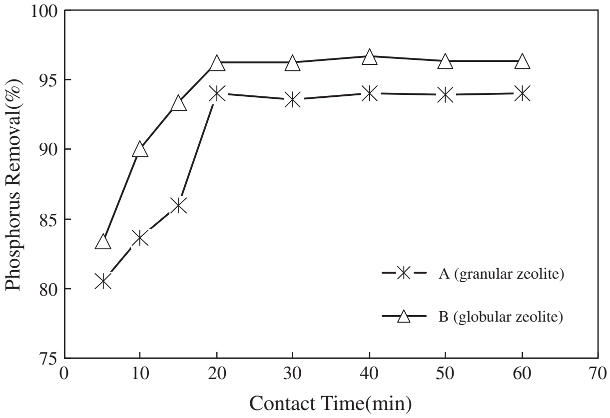

Fig. 4. Effect of reaction time on phosphorus removal for sorbents A and B.

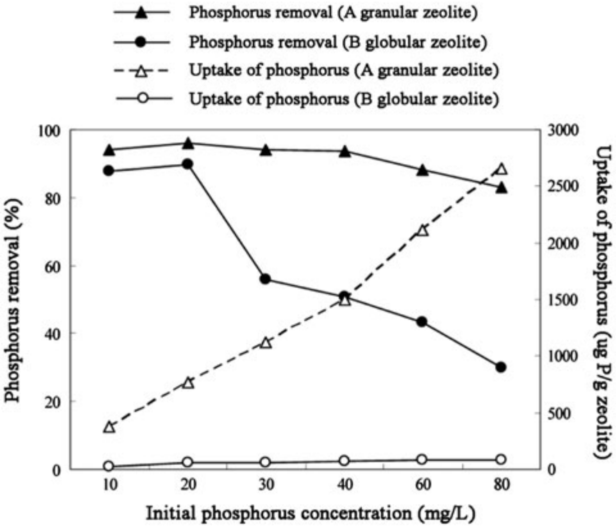

Fig. 5. Phosphorus removal and uptake at different initial phosphorus concentrations.

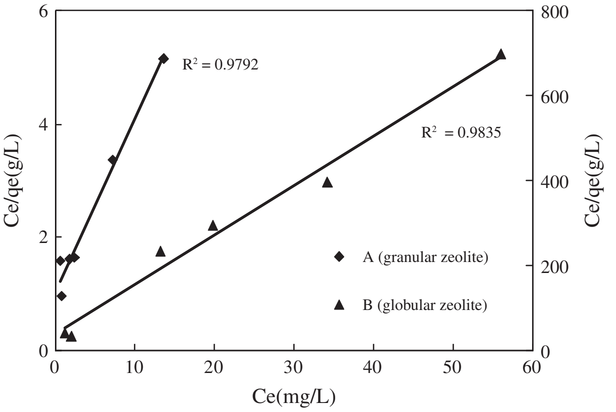

Fig. 6. Linearized form plot of Langmuir isotherm for phosphorus adsorption on A and B.

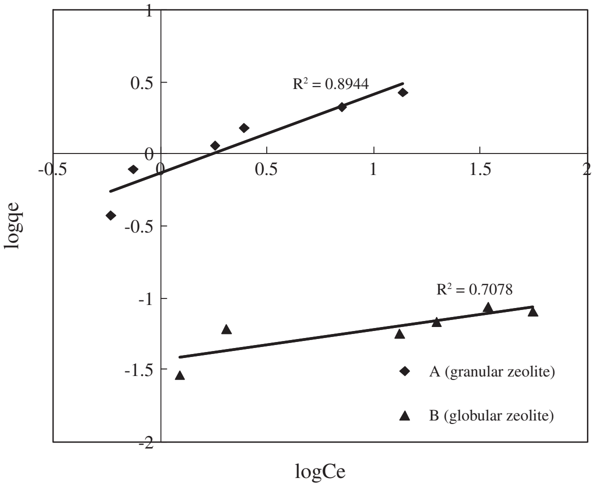

Fig. 7. Linearized form plot of Freundlich isotherm for phosphorus adsorption on A and B.

work is quite similar to that of zeolite used in other investigations [17]; at all phosphorus concentrations experiments, phosphorus removal reliability decreased with improving zeolite concentration, while at the same time the amount of phosphorus uptake increased. This may be a reflection of the correlation between the uptake of phosphorus and the ratio of initial phosphorus concentration. In terms of the loading curve of A, it changes much more steeply than B; yet in the light of phosphorus removal, it shows the opposite tendency. This is also implied that the size of sorbents impacts the behavior of adsorption courses. There are more adsorption sites in the sorbent surface at low phosphorus concentrations than that at high phosphorus concentrations, which can adsorb most of the phosphorus in this aqueous solution. Therefore, the results show that removal efficiency of phosphorus declines with phosphorus concentration increasing. The increasing tendency for phosphorus loading implies that these adsorption courses have not achieved adsorption equilibrium within tested phosphorus concentration.

3.5. Adsorption isotherm study

Adsorption isotherm experiments were carried out with the experimental procedure as for 3.4.

The adsorption isotherms were developed using the Langmuir and Freundlich models to describe adsorption behavior. Fig. 6 shows the linear form of the Langmuir model for various final phosphorus concentrations. Fig. 7 gives the Freundlich equilibrium

Table 4
Langmuir and Freundlich constants for phosphorus adsorption on the two sorbents

Sorbent	Freundlich constants			Langmuir constants		
	$1/n$	K (mg/g)	R^2	q^0 (mg/g)	b (L/mg)	R^2
A	0.548	0.732	0.8944	3.29	0.29	0.9792
B	0.211	0.0365	0.7078	0.086	0.32	0.9835

model of phosphorus adsorption onto A and B. The plot is linearized to obtain the Freundlich constants of 1/n and k from the slope and intercept.

The Langmuir and Freundlich parameters and correlation coefficients for the adsorption of phosphorus onto granular and globular zeolites are summarized in Table 4. The outcomes of this analysis conclude that the value of $1/n$ is 0.548 for A and 0.211 for B. This is in agreement with the past studies conducted in this area [18,19]. Furthermore, the $1/n$ parameter for Frenudlich model is a measure of exchange intensity or surface heterogeneity and ranges between 0 and 1. In this investigation, the values of $1/n$ for both species are less than 1 which suggest that the adsorption conditions are favorable [20,21]. K is a constant indicating the adsorption capacity of sorbent, with the value of 0.732 mg/g for sorbent A and 0.0365 mg/g for B, respectively. For the Langmuir equation, it is noted that q^0 is 3.29 mg/g for A and 0.086 mg/g for B and parameter b is 0.29 L/mg for A and 0.32 L/mg for B. Examination of Table 4, as well as Figs. 6 and 7, reveals that the Langmuir equilibrium model has a much better fit ($R^2 = 0.9792$, 0.9835) than that of the Freundlich model ($R^2 = 0.8944$, 0.7078). This result is in agreement with the findings of Chen et al. [22]. It is also implied that there is homogenous distribution of active sites on the surface of zeolites; the reason is that the Langmuir isotherm assumes that the surface of adsorbent is homogenous.

4. Conclusions

The results of this study provide experimental support for the efficiency of a low-cost technology for phosphorus removal from wastewater based on adsorption by zeolites. The results of this research support the following conclusions regarding performance of these two sorbents. The experimental procedure identified the following optimum conditions for phosphorus removal by the sorbents:

(1) for sorbent A (granular zeolite), pH of 1.8, sorbent dosage of 2.5 g per 100 mL solution, contact time of 20 min, and initial phosphorus concentration of 20 mg/L;

(2) for sorbent B (globular zeolite), pH of 2.0, dosage of 30 g per 100 mL solution, contact time of 40 min, and initial phosphorus concentration of 20 mg/L.

In terms of phosphorus uptake, A has performed better than B in all experimental scenarios. In terms of phosphorus removal efficiency, both A and B performed well (greater than 93% removed). However, the required dosage for B (30 g per 100 mL) is much greater than A (2.5 g per 100 mL).

The Langmuir isotherm model ($R^2 = 0.9792$, 0.9835) outranked the Freundlich model ($R^2 = 0.7078$, 0.8944) in fitting adsorption isotherms to experimental adsorption results.

In summary, this research investigates and illustrates the influence of a number of conditions on phosphorus adsorption by two varieties of zeolite, and identifies experimental optimum conditions for maximum phosphorus removal efficiency. The results of this research show relatively low uptake of phosphorus on these two kinds of zeolites. Therefore, seeking the proper modifier of zeolites for phosphorus removal would be the further work.

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