Research Article

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Synthesis of zeolite from fly ash and its adsorption of phosphorus in wastewater

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Abstract: Using synthetic zeolite from fly ash to treat high concentration phosphorus wastewater does not only improve the utilization of fly ash as solid waste but also reduce the environmental pressure caused by eutrophication. A synthetic zeolite was prepared from coal fly ash by one-step hydrothermal synthesis and applied for phosphorus adsorption from industrial wastewater (~8,000 mg-P/L), and its adsorption characteristics and performance were studied. The results indicated that the product was a well-crystallized Na-P1 zeolite with typical morphology of plate- and rod-shaped crystals. Compared with the original fly ash, the specific surface area and average pore volume of the synthetic zeolite were nine and six times larger than the fly ash, reaching 43.817 m²/g and 0.122 cm³/g. The results from phosphorus adsorption onto the synthetic zeolite showed that the synthetic zeolite had good phosphorus adsorption properties. The adsorption process highly conformed to the pseudo-second-order kinetic model with the regression coefficient R^2 of 0.998. Phosphorus adsorption on the synthetic zeolite was fitted to the Langmuir monolayer adsorption model, and the regression coefficient R^2

was 0.989. The maximum phosphorus adsorption capacity was 84.4 mg-P/g-zeolite.

Keywords: zeolite, hydrothermal synthesis, phosphorus wastewater, adsorption kinetics, adsorption isotherm

1 Introduction

Phosphorus is not only an essential nutrient element in all organisms but also plays an important role in the development of industry and agriculture, such as the production of chemical fertilizers, pesticides, detergents, and so on [1]. Large quantities of phosphorus wastewater is produced by industries, agricultural production, and daily life of humans. When a large amount of phosphorus wastewater is discharged into natural water, which increases the phosphorus content in water to above 0.02 mg/L, eutrophication will occur [2,3]. Algae and other aquatic plant life will flourish, resulting in a significant decrease in the dissolved oxygen content and the deterioration of water quality [4]. Algal blooms also lead to foul odors and bad flavor, and toxic algae (red tide) will kill the desirable fish and shrimps and even threatens the survival of human beings [4,5]. Moreover, the growth of macrophytes and phytoplankton is stimulated principally by phosphorus and nitrogen. The growth of rooted aquatic macrophytes will interfere with navigation, aeration, and channel capacity, and the dead macrophytes and phytoplankton will cause microbial breakdown processes [4,6]. To prevent water eutrophication, the US Environmental Protection Agency (EPA) recommends that if wastewater is discharged into lakes or reservoirs, the level of PO_4^{3-} should not be higher than 0.05 mg/L [7]. It is necessary to remove phosphorus from water and wastewater to meet more stringent environmental regulations [8].

Currently, the commonly used methods for phosphorus removal can be generally divided into physicochemical methods and biological methods. Physicochemical methods include chemical precipitation [9–11], ion exchange [12–14], adsorption [15–17], crystallization [18–20], and dissolved oxygen flotation [21], and biological methods mainly include

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enhanced biological phosphorus removal (EBPR) [22,23], microalgae phosphorus removal [24–26], and so on. A feasible method is necessary for removing phosphate from water to relieve eutrophication [27]. Among these techniques, adsorption by selective adsorbents is promising and the most attractive and efficient method for purification and separation of phosphate from water and wastewater [28,29]. It has the characteristics of low cost, flexible operation, and high selectivity [30].

With the continuous development of adsorbent research, zeolite with superior performance, which is relatively cheap and easy to obtain, has been widely studied and used in wastewater treatment. Zeolite is a kind of representative aluminosilicate mineral containing water and alkali (or alkaline-earth metal) [31]. All zeolites have a framework composed of silica and alumina tetrahedra, and each AlO_4 tetrahedra that is incorporated into zeolite lattice produces a net negative charge, which makes zeolites having permanent negative charge structure and the positively charged groups easily adsorbed on the zeolite surface by ion exchange [32,33]. In addition, there are many holes and channels inside zeolites, which lead to zeolites having huge internal surface areas ($400\text{--}800\text{ m}^2/\text{g}$ generally in natural zeolites [32,33], but less in synthetic zeolites). Although the specific surface area of natural zeolites is large, it is easily filled with water molecules and some impurities, which cause a low ion exchange capacity. Compared with natural zeolites, synthetic zeolites have smaller specific surface areas, but their ion exchange capacity is larger, and they are also rich in calcium, iron, and other components, which are conducive to adsorption [34]. Zeolites have large adsorption capacity, strong ion exchange capacity, high selectivity, and excellent thermal stability due to its unique pore structure and crystal chemical characteristics [35]. These physical and chemical properties are of great significance in phosphorus wastewater treatment.

Fly ash is an industrial solid waste with large emission, and its disposal has been faced with some problems such as inadequate technology utilization, low added value of products, and occupation of large areas of land [36]. However, owing to the similar main chemical components (SiO_2 and Al_2O_3) between fly ash and zeolite, it enables fly ash to be used in zeolite synthesis for phosphorus removal from wastewater. Many studies [37–40] show that zeolites synthesized from fly ash can show a good effect on the adsorption treatment of phosphorus wastewater. Moreover, once loaded with nutrients (such as phosphorus), zeolites can be applied as a fertilizer and a soil conditioner in agricultural industries [41,42]. It brings several associated benefits, such as increased

nutrient loading capacity, cost reduction, control of the nutrient release rate, adaptability to soil conditions, and higher water retention [42]. However, the synthetic zeolite from fly ash also has some disadvantages. The mechanical strength of the synthetic zeolite is not as good as that of adsorbents in previous studies [43–46]. Industrial production of the synthetic zeolite is also difficult.

Currently, most of the studies on phosphorus adsorption by synthetic zeolite from fly ash are based on synthetic simulated phosphorus water solutions; however, there is a relatively lack of research on complex actual phosphorus wastewater adsorption. Therefore, we aim to use the synthetic zeolite from fly ash to treat actual phosphorus wastewater to preliminarily explore its adsorption characteristics of phosphorus in wastewater. This does not only improve the utilization of fly ash resources but also reduce the environmental pressure caused by eutrophication. In this paper, fly ash was taken as a raw material and NaOH solution as an activator, and the specific zeolite was synthesized by the hydrothermal method at high temperature and a certain solid–liquid ratio. The physical and chemical properties of the synthetic zeolite were studied, and its adsorption performance for phosphorus in the actual phosphorus wastewater was analyzed, so as to provide a reference for the adsorption application of synthetic zeolite fly ash in actual phosphorus wastewater.

2 Materials and methods

2.1 Materials

2.1.1 Fly ash

The fly ash used in the experiment was collected from a coal-fired power plant in Hubei Province, China. The as-received sample was blended, divided into representative sample portions, dried, and stored in sample bags. X-ray fluorescence spectrum (XRF) was performed to analyze the chemical composition of fly ash, and the results are presented in Table 1. The fly ash mainly comprised SiO_2 and Al_2O_3 with small amounts of other impurities such as Fe_2O_3 and CaO [47–49].

2.1.2 Industrial phosphorus wastewater

The water sample was acquired from a phosphorus chemical plant in Yichang, Hubei Province. The chemical

Table 1: Chemical composition of fly ash and synthetic zeolite (wt%)

Element	Si	Al	Na	Fe	Ca	Ti	Zn	Other
Fly ash	21.06	15.19	0.12	6.18	4.15	1.54	0.53	2.95
Synthetic zeolite	19.30	13.58	6.37	5.17	3.61	1.29	0.44	1.74

composition of the water sample is presented in Table 2. The wastewater is strongly acidic (pH = 1.78) and complex. It contained high concentrations of phosphorus (about 8,000 mg/L) and other heavy metals.

2.1.3 Reagents

Additional reagents used for zeolite synthesis, chemical analysis of phosphate, and pH regulation included phenolphthalein indicator aqueous solution (1%), concentrated H_2SO_4 (AR, 95.0–98.0%), potassium persulfate $\text{K}_2\text{S}_2\text{O}_8$ (AR, $\geq 99.5\%$), sodium hydroxide NaOH (AR, $\geq 96\%$), concentrated HCl (AR, 36.0–38.0%), ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AR, $\geq 99.0\%$), ammonium metavanadate NH_4VO_3 (AR, $\geq 99.0\%$), and anhydrous KH_2PO_4 (AR, $\geq 99.5\%$). Ultrapure water was used throughout the experiment.

2.2 Method

2.2.1 Characterization of materials and determination of phosphorus

The crystal phase composition of the fly ash and synthesized zeolite samples was determined with a Bruker D8 ADVANCE X-ray diffractometer, $\text{CuK}\alpha$ radiation. The scanning range and speed were $10\text{--}80^\circ$ and $5^\circ/\text{min}$, respectively. The data were analyzed using MDI Jade 6.0 software.

A JSM5510LV scanning electron microscope from Japan Electronics Co., Ltd was used to study the surface morphology of the fly ash and the synthesized zeolite. The accelerating voltage of the instrument was 20 kV.

The specific surface area and pore volume of the fly ash and synthesized zeolite were determined using an ASAP 2020 HD 88 analyzer for specific surface area and porosity from American Micromeritics company. The experiment was conducted at 77.523 K with liquid nitrogen. Samples pretreatment procedure was as follows: the samples were degassed in a vacuum for 4 h at 120°C to remove the gas and water vapor adsorbed on the sample surface.

Table 2: Water quality composition of phosphorus wastewater

Parameter	Concentration (mg/L) (except pH)	Determination method
pH	1.78	Glass electrode method
Total P	7803.5	Vanadomolybdophosphoric acid colorimetric method
F	1,144	IC
Cl	456.5	IC
SO_4^{2-}	4124.5	IC
Na	1,056	ICP-MS
Ca	1266.9	ICP-MS
Si	200.3	ICP-MS
Cr	0.96	ICP-MS
Mn	49.9	ICP-MS
Fe	51	ICP-MS
Ni	2.47	ICP-MS
Cu	0.72	ICP-MS
Zn	8.43	ICP-MS
Pb	0.21	ICP-MS

The wastewater characteristics were determined, and the results are presented in Table 2. The pH of the water sample was determined with a glass electrode method using the PHSJ-4F pH meter from Shanghai Leici. The total phosphorus concentration was determined by the ASTM ammonium molybdate method [50] and by analyzing the sample on a 752 N UV-Vis spectrophotometer from Shanghai Yidian. Dionex ICS-1500 ion chromatograph was used to analyze the concentrations of F^- , Cl^- , and SO_4^{2-} , while an Agilent 7700 ICP-MS was used to determine the concentrations of metal elements in the wastewater.

2.2.2 Zeolite synthesis from fly ash

The synthetic zeolite was prepared using an adapted synthesis method developed by Wu et al. [51]. 70 g of dried fly ash and 175 mL of 2 mol/L NaOH solution were placed in a 250 mL PTFE lined stainless steel autoclave reactor (solid–liquid ratio of 1 g:2.5 mL). The slurry was mixed well using a glass stirring rod, the reactor was sealed, and the hydrothermal synthesis was performed for 24 h at 120°C . After the reaction was completed, the reactor was allowed to cool naturally to room temperature, and the product was removed from the reactor and washed repeatedly with deionized water until the pH of the supernatant was nearly neutral. The slurry was filtered and the solid was dried at 105°C for 18 h. The conglomerated solid product was broken up in a mortar and pestle to obtain a well-mixed powder product.

2.2.3 Adsorption experiment of actual phosphorus wastewater

2.2.3.1 Adsorption kinetics

300 mL of the industrial phosphorus wastewater (pH value was about 1.8) and 15 g of synthetic zeolite were added into a 500 mL beaker. The slurry was stirred for 30 h at 30°C and 200 rpm. 3 mL sample was taken at different time intervals and was centrifuged in a high-speed centrifuge at 1,500 rpm. The supernatant was used to determine the total phosphorus concentration using the vanadomolybdophosphoric acid colorimetric method [50].

2.2.3.2 Adsorption isotherm

The industrial phosphorus wastewater sample was diluted in the proportion of 1, 1/2, 1/4, 1/8, and 1/16 to different initial concentrations for the adsorption process, and before adsorption, the pH values of all water samples were adjusted to be 1.8. Then, 2.5 g of synthetic zeolite was added to 50 mL of these wastewater samples at different initial concentrations in 100 mL conical flasks with grounded glass lids. The samples were shaken in a thermostatic oscillator water bath at 180 rpm and 30°C for 8 h. After adsorption, the samples were filtered, and the supernatant of each was used to determine the total

phosphorus concentration by the vanadomolybdophosphoric acid colorimetric method [50].

The phosphorus removal and adsorption capacity are determined using Eqs. 1 and 2, respectively:

$$R = \frac{C_0 - C_e}{C_0} \times 100\%, \quad (1)$$

$$Q = \frac{(C_0 - C_e)V}{1,000 \times m} \quad (2)$$

where R represents phosphorus removal (%); C_0 and C_e are the mass concentrations of phosphorus initially and at equilibrium, respectively mg-P/L; Q is the adsorption capacity of phosphorus (mg-P/g-zeolite); V is the volume of wastewater (mL); and m is the mass of synthetic zeolite (g).

3 Results and discussion

3.1 XRD analysis of synthetic zeolite

The difference in the crystal structure between fly ash and the synthesized zeolite can be observed from the XRD patterns shown in Figure 1. The main crystalline components of raw fly ash were quartz (SiO_2) and hematite (Fe_2O_3). After hydrothermal synthesis, most of the characteristic peaks of quartz and hematite disappeared. Among the series, diffraction peaks of synthetic zeolite,

Figure 1: XRD patterns of fly ash and synthetic zeolite.

Figure 2: SEM photos of (a and b) fly ash and (c and d) Na-P1 zeolite at different magnifications.

regular, sharp, and strong peaks were present at 12.5° , 17.7° , 21.7° , 28.1° , and 33.4° , which were in good agreement with the characteristic peaks of Na-P1 zeolite ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$). In addition, according to the comparison of characteristic peaks, the product still contained a small amount of quartz. This showed that in the alkaline medium, quartz and hematite in fly ash were dissolved, and most of the quartz and mullite were transformed into well-crystallized zeolite materials. A small amount of dissolved quartz remains after 24 h of hydrothermal synthesis.

3.2 SEM analysis of the morphology of synthetic zeolite

The SEM pictures of fly ash and synthetic zeolite are shown in Figure 2. Fly ash particles were spherical and amorphous with the loose structure. The surfaces of these particles were rough, with either distributed pores of different sizes or adhered smaller particles. Previous studies found that during the hydrothermal synthesis process, quartz, amorphous silicon, and aluminum materials

on the fly ash particle surface dissolve in the alkaline environment to form the zeolite crystal precursor and finally form zeolite crystal [52,53]. From the SEM pictures of the synthetic zeolite (Figure 2c and d), it can be observed that fly ash lost its original particle shape and the rough surface transformed into various shapes of crystals, such as plate and rod, which accorded well with the morphology of Na-P1 zeolite [54] and the phase analysis of XRD.

3.3 Analysis of specific surface area and pore volume of synthetic zeolite

The specific surface area and pore size distribution of an adsorbent determine the contact between the target pollutants and the surface-active groups of the adsorbent, which are the key factors affecting the adsorption performance [55]. The adsorption and desorption isotherms of N_2 at low temperature and pore size distribution of fly ash and Na-P1 zeolite are shown in Figure 3. Although the adsorption curves of fly ash and Na-P1 zeolite were slightly different, both conformed to the type II isotherms

Figure 3: Adsorption–desorption isotherms and pore size distribution of (a) fly ash and (b) Na-P1 zeolite.

as per the International Union of Pure and Applied Chemistry (IUPAC) classification, which generally presented the inverse “S” shape. At low relative pressure ($P/P_0 = 0-0.3$), the curves rose slowly and were slightly convex upward, which the adsorption of N_2 by fly ash and Na-P1 zeolite changed from monolayer to multilayer. With the relative pressure ascending ($P/P_0 = 0.3-0.8$), the adsorption capacity of N_2 increased slowly, which showed that the interaction between the solids and N_2 was weak. When the system transferred from medium to high

relative pressure, the adsorption capacity had a steep rise and no adsorption saturation occurred near the saturation vapor pressure. At the same time, the adsorption curve and desorption curve did not completely coincide, but formed a hysteresis loop with a certain area, indicating that both fly ash and Na-P1 zeolite contained a certain amount of mesopores and capillary condensation occurred. Different shapes of hysteresis loops reflect certain pore structure characteristics and types. The adsorption and desorption curves of fly ash and Na-P1 zeolite were similar to the type H3 hysteresis loop, which indicated that there were slit-shaped pores aggregated by plate-like particles and other pores with various shapes, which were consistent with the morphology shown in SEM images.

Comparing the pore size distribution of fly ash and Na-P1 zeolite, it can be seen that the pore volume density of fly ash and Na-P1 zeolite reached maximum values at about 20 and 5 nm, respectively, and the peak of Na-P1 zeolite was narrower, which indicated that the pore size of the synthetic zeolite became smaller and more homogeneous. It can be seen from Table 3 that after hydrothermal synthesis, the specific surface area and average pore volume of fly ash improved significantly from 4.4713 m^2/g and 0.019523 cm^3/g to 43.817 m^2/g and 0.122088 cm^3/g , respectively, an increase of nine and six times, respectively. The increase of the specific surface area when synthetic zeolite particles are formed is beneficial to phosphate adsorption and precipitation reaction [56], which can improve the adsorption performance of the synthetic zeolite for phosphorus.

3.4 Effect of adsorption time on phosphorus adsorption by synthetic zeolite and the adsorption kinetics

By using the synthetic zeolite to treat actual phosphorus wastewater, the phosphorus removal performance changed with time as shown in Figure 4. The phosphorus removal efficiency and adsorption capacity of synthetic zeolite gradually increased with the extension of adsorption time. When the adsorption progressed to 8 h, the phosphorus

Table 3: Comparison of parameters of fly ash and Na-P1 zeolite

Parameter	Specific surface area (m^2/g)	Average pore size (nm)	Average pore volume (cm^3/g)
Fly ash	4.4713	32.7812	0.019523
Na-P1 zeolite	43.8170	11.2567	0.122088

removal efficiency of synthetic zeolite increased up to 38.3% and the corresponding phosphorus adsorption capacity increased to 59.8 mg-P/g. After 8 h, the phosphorus adsorption by the synthetic zeolite basically reached equilibrium, and the removal efficiency and adsorption capacity of phosphorus were stabilized at about 38% and 60 mg-P/g, respectively. At the beginning of the adsorption, a large amount of phosphorus was adsorbed in a short time due to the large phosphorus concentration difference at the solid-liquid interface in the system, and the resulting hydraulic mass transfer force [57], which made the phosphorus removal efficiency and adsorption capacity of the synthetic zeolite to increase rapidly. When the adsorption time was extended from 8 to 30 h, most of the adsorption sites on the synthetic zeolite were occupied and the phosphorus concentration gradient in wastewater decreased gradually, which led to the stabilization of phosphorus removal efficiency of synthetic zeolite. The observed fluctuation of the phosphorus removal effect after the adsorption equilibrium may be due to experimental environmental factors. The optimum adsorption time of synthetic zeolite was 8 h.

Pseudo-first-order kinetics and pseudo-second-order kinetics are common kinetic models. To further evaluate the adsorption characteristics of synthetic zeolite for phosphorus removal in wastewater, this study used these two models to analyze the kinetic characteristics of the phosphorus adsorption reaction. The two model equations are shown in Eqs. 3–5.

(1) Pseudo-first-order kinetic equation:

$$Q_t = Q_e [1 - \exp(-k_1 t)], \quad (3)$$

where Q_t is the adsorption capacity at a certain time (mg/g); Q_e is the adsorption capacity at equilibrium

(mg/g); k_1 is the adsorption rate constant of pseudo-first-order kinetics (h^{-1}); and t is the reaction time (h).

(2) Pseudo-second-order kinetic equation:

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t}. \quad (4)$$

This kinetic equation can also be expressed as a linear equation as per Eq. 5:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}, \quad (5)$$

where Q_t is the adsorption capacity at a certain time (mg/g); Q_e is the adsorption capacity at equilibrium (mg/g); k_2 is the adsorption rate constant of pseudo-second-order kinetics ($\text{g}/(\text{mg h})$); t is the reaction time (h); and k_2 and theoretical Q_e can be calculated by plotting t and t/Q_t , respectively.

The fitted adsorption kinetics curves of phosphorus are shown in Figures 5 and 6. Table 4 presents the kinetic parameters and regression coefficients (R^2) obtained from the nonlinear fitting between the values of Q_t and t and the linear fitting between t/Q_t and t . The results showed that the adsorption of phosphorus by the synthetic zeolite was more in line with the pseudo-second-order kinetics with the regression coefficient of 0.998, and the fitted equilibrium adsorption capacity Q_e value was close to the actual adsorption value, which indicated that the adsorption process of phosphorus was controlled by chemical adsorption [58]. In this experiment, the pH value of the actual phosphorus wastewater was about 1.8, which indicated that the wastewater was strongly acidic. At this

Figure 4: Effect of time on phosphorus removal.

Figure 5: The pseudo-first-order kinetic fitting of phosphorus adsorption on synthetic zeolite.

Table 4: The kinetic fitting parameters of phosphorus adsorption on synthetic zeolite

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Q_e (mg-P/g)	k_1 (h ⁻¹)	R^2	Q_e (mg-P/g)	k_2 (g/mg h)	R^2
57.41	18.44	0.072	60.24	0.09	0.998

pH, the proton donating species in water were H_3PO_4 or $H_2PO_4^-$. Therefore, the adsorption of phosphorus by the synthetic zeolite can be expressed by Eqs. 6 and 7:

Moreover, the metal ions (such as Ca^{2+} , Fe^{3+} , and Fe^{2+}) in the synthetic zeolite will dissolve and form phosphate precipitation with H_3PO_4 and $H_2PO_4^-$ in water.

3.5 Effect of initial concentration on phosphorus adsorption by synthetic zeolite and the adsorption isotherm

The phosphorus removal efficiency and adsorption capacity of the synthetic zeolite for phosphorus wastewater with different initial concentrations are shown in Figure 7. The results show that with the increase of initial phosphorus concentration, the phosphorus removal efficiency increased

first and then declined, while the adsorption capacity kept increasing. Overall, the phosphorus removal efficiency by the synthetic zeolite was above 35% for 500–8,000 mg/L of phosphorus wastewater. When the initial concentration increased from 500 to 2,000 mg/L, the phosphorus removal efficiency increased up to 57.6%, and once the initial concentration changed from 2,000 to 8,000 mg/L, it decreased significantly. This indicated that the synthetic zeolite had more vacant adsorption active sites at lower initial concentration; however, if the initial concentration of phosphorus wastewater exceeded a certain value, most of the active sites were occupied, which resulted in the decline of removal efficiency.

To preliminarily explore the adsorption behavior and mechanism of phosphorus on synthetic zeolite, two commonly used isothermal adsorption models were considered to fit and analyze the adsorption characteristics of synthetic zeolite – the Langmuir and Freundlich adsorption isotherms. The isothermal adsorption models are specifically shown in Eqs. 8–10.

(1) Langmuir isotherm equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

The separation constant R_L of the adsorption reaction can be further obtained from the Langmuir equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where Q_e and Q_m are the equilibrium and saturated adsorption capacity per unit weight of adsorbent (mg/g), respectively; C_0 and C_e are the initial and equilibrium mass concentration of phosphorus in

Figure 6: The pseudo-second-order kinetic fitting for phosphorus adsorption on synthetic zeolite. **Figure 7:** Effect of initial concentration on phosphorus removal.

Figure 8: The isothermal adsorption fitting curves of phosphorus on synthetic zeolite.

wastewater (mg/L), respectively; K_L is the Langmuir constant (L/mg), which is related to the binding site affinity [54]; R_L is a separation constant of dimension 1 in the Langmuir adsorption model, which is used to describe the adsorption performance of adsorbent. When $R_L < 1$, the adsorption process is considered to be beneficial, and if $R_L > 1$, the adsorption process is nonbeneficial.

(2) Freundlich isotherm equation:

$$Q_e = K_F C_e^{\frac{1}{n}}, \quad (10)$$

where K_F and $1/n$ are the Freundlich adsorption equilibrium constants, which represent the affinity coefficient and adsorption strength, respectively. When $0 < 1/n < 1$, the adsorption process is beneficial.

The fitted curves of the isothermal adsorption models are shown in Figure 8, and Table 5 presents the adsorption parameters and regression coefficients (R^2) obtained from the nonlinear fitting between the values of Q_e and C_e . The regression coefficients of Langmuir and Freundlich isotherms were 0.989 and 0.959, respectively. Compared with the Freundlich isotherm, the Langmuir isotherm had a higher fitting correlation. Therefore, the isothermal adsorption of phosphorus by the synthetic

zeolite was better fitted to the Langmuir isotherm. The phosphorus adsorption on synthetic zeolite was a uniform monolayer, and the maximum phosphorus adsorption capacity was 84.4 mg/g. According to Table 5, the separation constant R_L of the Langmuir isotherm ranged from 0.257 to 0.849 and the Freundlich isotherm constant $1/n$ was 0.6045, meeting the limits of $0 < R_L < 1$ and $0 < 1/n < 1$, which indicated that the adsorption process of the synthetic zeolite for phosphorus was beneficial adsorption and the synthetic zeolite had good adsorption performance for phosphorus.

Table 6 presents the maximum phosphate adsorption capacity of the zeolite adsorbent reported in the previous literature and that prepared in this study. According to Table 6, it can be roughly determined that the synthetic zeolite prepared in this study is an adsorbent with high phosphorus adsorption capacity. This indicates that the zeolite synthesized from fly ash has a broad prospect in phosphate removal from wastewater. In addition, due to the complex composition of actual phosphorus wastewater, which contains a variety of anions (such as arsenic, phosphate, and nitrite), the selectivity trend of adsorbents for these ions completely depends on the Hofmeister series. Adsorbents prefer low hydrated anions to high hydrated ones so long as the charge number of anions is equal as that pointed out in the previous studies [12,15–17,27,43]. Therefore, in the future research, except for studying the influence of the structure and composition of synthetic zeolite, adsorption time, and initial phosphorus concentration on the adsorption performance, other influencing factors such as coexisting ions in wastewater, pH of wastewater, and zeolite dosage should also be studied. The reusability of the synthetic zeolite also needs to be explored.

4 Conclusion

In this study, Na-P1 zeolite was hydrothermally synthesized from fly ash for phosphorus removal in wastewater. The adsorption kinetics and isotherm experiments were carried out to determine the adsorption performance of the synthetic zeolite. The characterization of the zeolite indicated that the crystal form of Na-P1 zeolite was intact,

Table 5: The isothermal adsorption fitting parameters of Langmuir and Freundlich

Q_m (mg-P/g)	Langmuir			Freundlich		
	K_L	R^2	R_L	K_F	$1/n$	R^2
84.436	3.7996×10^{-4}	0.989	0.257~0.849	0.332	0.6045	0.959

Table 6: Comparison of phosphorus adsorption capacity of various zeolite adsorbents

Material	Maximum phosphorus adsorption capacity (mg/g)	References
Na-ZFA	35.31	Wu et al. [34]
HC-Z	87.51	Ji et al. [38]
ZXH	149	Bonetti et al. [42]
ZFA	11.79–47.17	Chen et al. [56]
La-P1	58.2	Goscianska et al. [59]
HUD Zeolite	79.4	Onyango et al. [60]
NaP1-FA	57 ± 5	Hermassi et al. [61]
Z-Fe	3.4 ± 0.2	Guaya et al. [62]
ZFA	84.44	Present study

and its specific surface area and average pore volume increased significantly, which were nine and six times of that of fly ash, respectively. This change can improve the phosphorus adsorption performance of the synthetic zeolite. In the adsorption kinetics study, the phosphorus uptake by the synthetic zeolite increased gradually with the extension of adsorption time and stabilized after 8 h. The adsorption process was well fitted to pseudo-second-order kinetics, and the regression coefficient (R^2) was 0.998. Adsorption isotherm study showed that the equilibrium phosphorus uptake increased followed by a sharp decrease in the increase of initial concentration. The Langmuir model can well explain the phosphorus adsorption on the synthetic zeolite, and R^2 was 0.989. It indicated that the phosphorus adsorption on the synthetic zeolite was dominated by monolayer chemical adsorption. The maximum phosphorus adsorption capacity calculated was 84.4 mg/g. The synthetic zeolite in this study showed a high phosphorus adsorption capacity and was promising in phosphate removal from wastewater.

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