



# Ammonia-nitrogen and phosphates sorption from simulated reclaimed waters by modified clinoptilolite

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## HIGHLIGHTS

- ▶ The salt and thermally modified clinoptilolite can effectively sorb NH<sub>3</sub>-N and phosphates.
- ▶ The phosphorus and nitrogen removal was consistent with Langmuir isotherm model.
- ▶ The modified clinoptilolite possesses rapid adsorption and slow balance characteristics.
- ▶ The adsorption is more in line with the Elovich adsorption dynamics equation.
- ▶ The entropy effect plays the role of the main driving force in the adsorption.

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## ABSTRACT

This paper presents the investigation of the ammonia-nitrogen and phosphates sorption from simulated reclaimed wastewater by modified clinoptilolite. The results showed that the modified clinoptilolite has a high sorption efficiency and removal performance. The ammonia-nitrogen and phosphates removal rate of the modified clinoptilolite reached to 98.46% and 99.80%, respectively. The surface of modified clinoptilolite became loose and some pores appeared, which enlarged the specific surface area; the contents of Na and Fe increased, and the contents of Ca and Mg decreased. The modified clinoptilolite possesses rapid sorption and slow balance characteristics and ammonia-nitrogen and phosphates sorption is more consistent with the Langmuir isotherm model. The adsorption kinetics of ammonia-nitrogen and phosphates follows the Elovich adsorption dynamics equation, which describes the sorption of ammonia-nitrogen and phosphates in aqueous solution as mainly a chemical sorption. Results from the thermodynamics experiment involving ammonia-nitrogen and phosphates sorption reveal that the process is a spontaneous and endothermic process, and is mainly driven by entropy effect.

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## 1. Introduction

In many countries, eutrophication is the main water pollution problem of lakes, water reservoirs, oceans, and the like [1]. In order to solve the eutrophication problems induced by the traditional secondary biological effluent and realize reuse of wastewater, which reduces sewage discharge and improves water shortage conditions, studies of sewage treatments in many countries have been done, especially those involving the removal of nitrogen and phosphorus [2,3].

The main methods of removing nitrogen and phosphorus include precipitation, crystallization, biological removal, and adsorption and ion exchange [4–7]. The adsorption and ion

exchange technology is a more effective way to remove nitrogen and phosphorus, due to its advantages, namely small floor area, simple process, and high efficiency, among others. In effect, finding new efficient materials that may be used for adsorption and ion exchange became a research highlight [8]. The natural zeolite, which are aluminosilicates containing a number of channels in their structure, have large adsorption ratio surface area comparing to other mineral materials. In recent years, researchers focused on sorbents based on zeolites. Natural zeolites are an abundant cation exchange material that is economically feasible for water and wastewater treatment. For example, the cation exchange capacity of Dogantepe zeolite was found to be 164.62 mequiv./100 g [9]. However, natural zeolites have deficiencies in the processing of some wastewaters, such as recycled water. In order to get more efficient treatment effects, natural zeolites are usually modified. The modification methods of natural zeolites include the acid- and alkali-treatment as well as, the salt-, thermal-, surfactant- and microwave modification [10,11]. However, only a few studies

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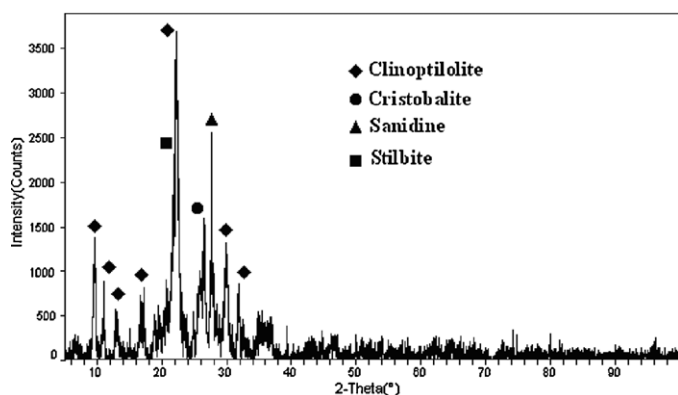


Fig. 1. XRD pattern of the natural zeolite.

on sorption mechanism have been conducted [12]. In the current study, the salt ( $\text{NaCl}$  and  $\text{FeCl}_3$ ) and thermal modification of zeolite was used to treat the simulated reclaimed waters and the adsorption mechanism of  $\text{NH}_3\text{-N}$  and P were studied.

## 2. Materials and methods

### 2.1. Materials

The zeolitic material, which had particle size range from  $50\text{ }\mu\text{m}$  to  $74\text{ }\mu\text{m}$ , was supplied by Jiekun Zeolite New Technology Processing Co., Ltd. in Xuanhua, Hebei province. The mineralogical composition of zeolite was determined as 80% clinoptilolite, 15% feldspar  $[(\text{Na}, \text{K}, \text{Ca})\text{AlSi}_3\text{O}_8]$ , and 5% quartz  $[\text{SiO}_2]$ . The XRD pattern of the material is given in Fig. 1. The main component of the natural zeolite was clinoptilolite associated with cristobalite, sanidine and stilbite.

### 2.2. Water sample

According to the condition of the reclaimed water, the simulated wastewater sample was prepared containing ammonia-nitrogen and phosphates of  $20\text{ mg/L}$  and  $5\text{ mg/L}$  respectively. The reagents used in this experimental work were ammonium chloride and dipotassium hydrogen phosphate. The pH value of water sample was adjusted to 6.0.

### 2.3. Modification of the natural zeolite

Modification experiments were carried out in  $300\text{ mL}$  flasks containing  $2\text{ g}$  of natural zeolite and  $100\text{ mL}$  2%  $\text{NaCl}$  solution, flasks were maintained at  $25^\circ\text{C}$  and shaken at  $200\text{ rpm}$  for  $2\text{ h}$ . Secondly, the zeolite modified by  $\text{NaCl}$  was dried at  $105^\circ\text{C}$  and then treated for  $1\text{ h}$  by  $0.4\%$   $\text{FeCl}_3$  solution. Finally, the modified zeolite was calcinated at  $200^\circ\text{C}$  in muffle furnace for  $1\text{ h}$  and cooled in closed container. Then clinoptilolite was kept, a after the end of the modification procedure, in dry place.

### 2.4. Sorption experiment

Water samples containing  $20\text{ mg/L}$  of ammonia-nitrogen and  $5\text{ mg/L}$  of phosphates were prepared at  $25^\circ\text{C}$ . The  $400\text{ mL}$  flasks containing the water samples and  $0.5\text{ g}$  of modified clinoptilolite were rotated for some time in a thermo stated rotator ( $30^\circ\text{C}$ ,  $200\text{ rpm}$ ) in order to achieve sorption equilibrium.

### 2.5. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) experiments

SEM and EDS experiments were conducted to provide information about the morphology and elemental composition of the natural and modified clinoptilolite, respectively.

### 2.6. Sorption isotherm experiment

Water samples containing  $5, 10, 20, 40, 50, 70, 100$ , and  $150\text{ mg/L}$  of ammonia-nitrogen and phosphates were prepared. First, the water samples and  $0.5\text{ g}$  of modified clinoptilolite were placed in several  $400\text{ mL}$  flasks. The flasks were then placed in a constant temperature oscillator for some time at  $30^\circ\text{C}$  and  $200\text{ rpm}$  rotational speed to achieve sorption equilibrium. Then the solution was filtered using a  $0.45\text{ }\mu\text{m}$  filter membrane and the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured. Total amount of adsorbed ammonia-nitrogen and phosphates were divided by the dry weight of zeolite to find out the average amount adsorbed, which were plotted against effluent ammonia-nitrogen and phosphates concentrations to show isotherm tests.

### 2.7. Adsorption kinetics experiment

Approximately  $1.5\text{ g}$  of modified clinoptilolite was weighed. The sample was placed in a  $1000\text{ mL}$  solution with  $6.0\text{ mg/L}$  ammonia-nitrogen and  $1.5\text{ mg/L}$  phosphates. The solution was stirred with speed of  $300\text{ rpm}$ . The solution was then filtered using a  $0.45\text{ }\mu\text{m}$  filter membrane and the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured.

### 2.8. Adsorption thermodynamics experiment

This experiment was conducted in flasks were then placed in a constant temperature oscillator Four equally weighed samples of modified clinoptilolite were placed in a  $250\text{ mL}$  solution with  $6.0\text{ mg/L}$  ammonia-nitrogen and  $1.5\text{ mg/L}$  phosphates. The individual samples were utilized in sorption experiments performed at  $20.0, 25.0, 30.0$ , and  $35.0^\circ\text{C}$ . At the end of the sorption experiment, the solution was filtered using a  $0.45\text{ }\mu\text{m}$  filter membrane, and then the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured.

### 2.9. Nitrogen and phosphates determination method

The phosphates and ammonia-nitrogen content of the water samples was determined using the ammonium molybdate and the Nessler reagent spectrophotometric methods.

## 3. Results and discussion

### 3.1. Results of the sorption experiment

After  $3\text{ h}$  sorption, the residual ammonia-nitrogen and phosphates content were  $0.80\text{ mg/L}$  and  $0.01\text{ mg/L}$ ; the ammonia-nitrogen and phosphates removal rate reached to  $98.46\%$  and  $99.80\%$ , respectively, which had reached equilibrium. Now the pH value changed to  $7.5$  from the initial  $6.0$  induced by the hydroxyl on the sorbent releasing into the solution. The observation indicates that the zeolite modified by  $\text{NaCl}$ -,  $\text{FeCl}_3$ - and thermal treatment has high ammonia-nitrogen and phosphates removal efficiency. The reasons are as follows.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  could be replaced by  $\text{Na}^+$  ions during the  $\text{NaCl}$ -treatment. The ionic radius of  $\text{Na}^+$  is shorter than that of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , so the effective aperture and exchange capacity of the modified zeolite increased. The ammonia-nitrogen

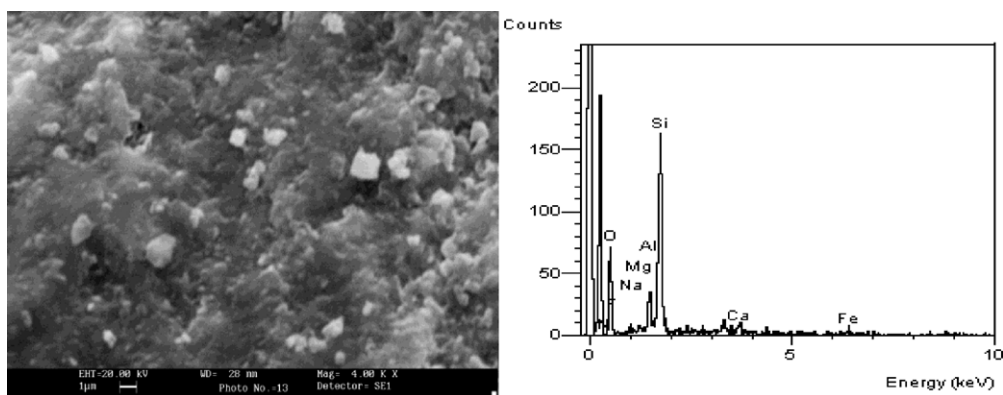


Fig. 2. SEM image and EDS patterns of natural zeolite (2000×).

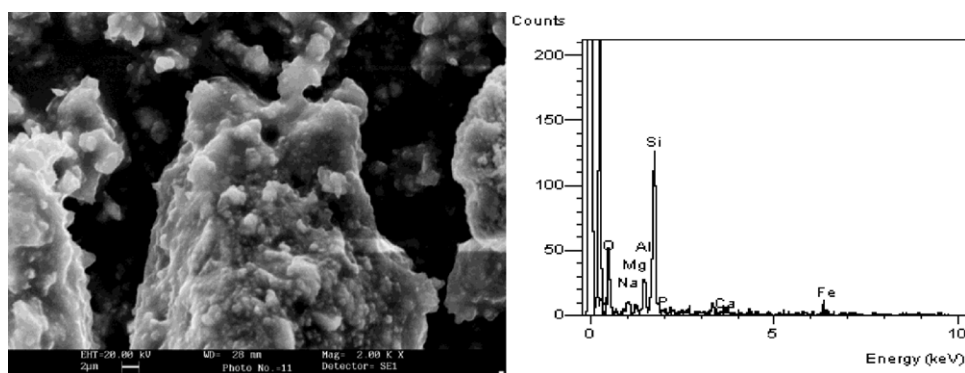


Fig. 3. SEM image and EDS patterns of modified clinoptilolite (2000×).

Table 1

Results of surface spectrum analysis of row natural zeolite and modified clinoptilolite.

Element	Row natural zeolite (wt/%)	Modified clinoptilolite (wt/%)
Na	3.80	4.51
Mg	1.28	0.55
Al	11.23	12.07
Si	76.38	77.12
Ca	5.62	3.29
Fe	1.69	2.46
Total	100.00	100.00

removal effects of the modified clinoptilolite improved. Hydrus iron oxide was formed on the surface of modified clinoptilolite obtained by  $\text{FeCl}_3$  and thermal treatment. The hydroxyl groups on the hydrous iron oxide exchange with  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  in the water sample, so the phosphate ions adsorbed to the modified clinoptilolite. The advantage of the modified clinoptilolite reported in this study is high efficiency for the simultaneous nitrogen and phosphorus removal.

### 3.2. SEM and EDS analysis

The SEM and EDS results of natural and modified clinoptilolite were compared. SEM images of the natural zeolite and modified zeolite are shown in Figs. 2 and 3, respectively. The figures show that the surface of raw natural zeolite is much smoother than that of the modified one. In addition, the surface of the modified clinoptilolite is dispersed and pores are present increasing its specific surface

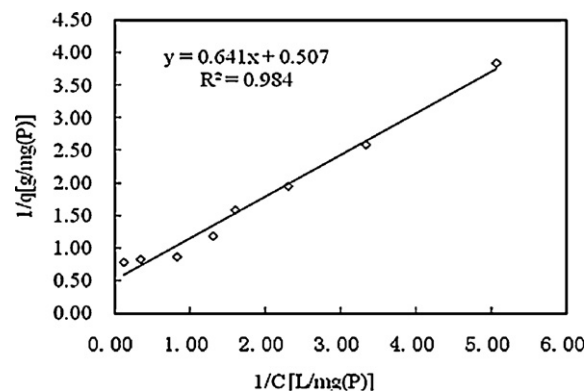


Fig. 4. Phosphorus Langmuir adsorption curve of modified clinoptilolite.

area. The results of surface spectrum analysis of row natural zeolite and modified clinoptilolite are shown in Table 1.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (1)$$

On the other hand, the Freundlich adsorption isotherm model is expressed as:

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (2)$$

The Langmuir and Freundlich adsorption isotherms of modified clinoptilolite absorbing ammonia-nitrogen and phosphates are shown in Figs. 4–7 respectively (Table 2).

The experiment results showed that the correlation coefficient of Langmuir adsorption is higher than that of the Freundlich adsorption. The ammonia-nitrogen and phosphorus adsorption isotherms

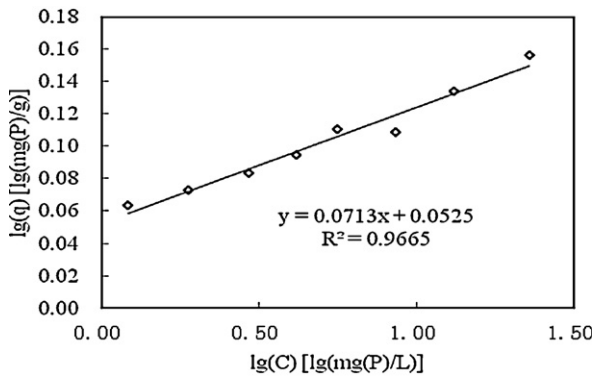


Fig. 5. Phosphorus Freundlich adsorption curve of modified clinoptilolite.

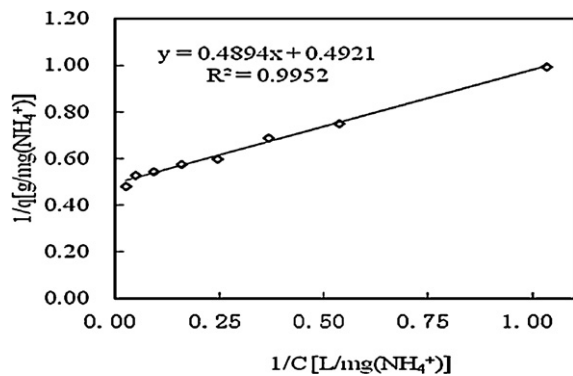


Fig. 6. Ammonia-nitrogen Langmuir adsorption curve of modified clinoptilolite.

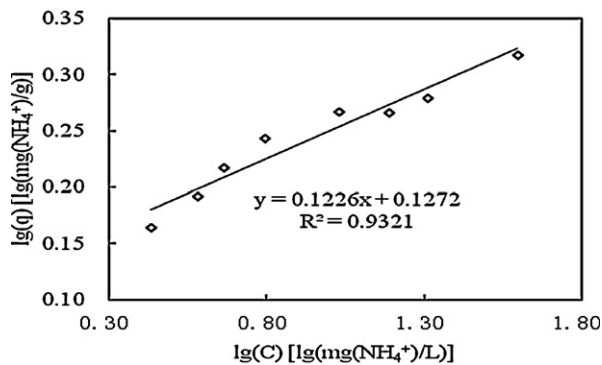


Fig. 7. Ammonia-nitrogen Freundlich adsorption curve of modified clinoptilolite.

are well-reproduced to the Langmuir adsorption isotherm model, which means that the phosphorus adsorption type of modified clinoptilolite involves multilayer coating. In addition, phosphorus adsorption is  $1/n=0.4447$  and ammonia-nitrogen adsorption is  $1/n=0.112$ . Using simple math, it can be shown that  $n > 1$ . This

**Table 2**  
Fitting parameters of Langmuir adsorption isotherm and Freundlich adsorption isotherm.

Items	$k$	$n$	$R^2$
Langmuir adsorption isotherm of phosphorus	0.641	0.507	0.984
Freundlich adsorption isotherm of phosphorus	0.071	0.052	0.966
Langmuir adsorption isotherm of ammonia-nitrogen	0.489	0.492	0.995
Freundlich adsorption isotherm of ammonia-nitrogen	0.122	0.127	0.932

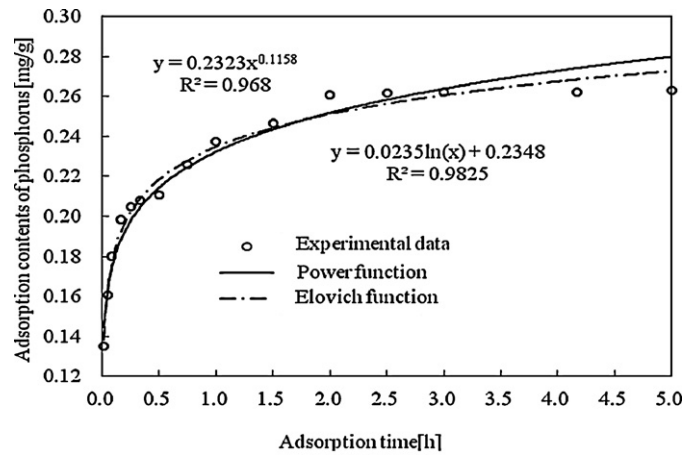


Fig. 8. Phosphorus adsorption kinetics curve of modified clinoptilolite.

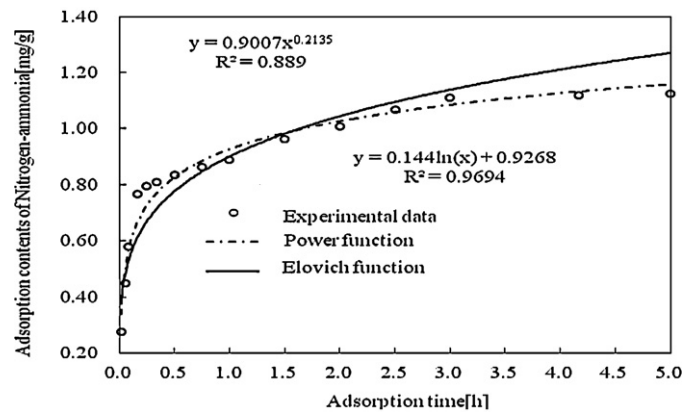


Fig. 9. Ammonia-nitrogen adsorption kinetics curve of modified clinoptilolite.

condition means that the experimental conditions helped the modified clinoptilolite to adsorb ammonia-nitrogen and phosphorus.

### 3.3. Adsorption kinetics of modified clinoptilolite absorbing ammonia-nitrogen and phosphorus

Experiments regarding the modified clinoptilolite adsorption kinetics of ammonia nitrogen and phosphorus were conducted to investigate the variation pattern of the two compounds. The results are shown in Figs. 8 and 9.

Figs. 8 and 9 show that the characteristics of ammonia-nitrogen and phosphorus adsorption of modified clinoptilolite is fast adsorption and slow balance, as time passes. The adsorption reaction continued for 120 min, thus, the concentration of phosphorus in the effluent was lower than 0.2 mg/L. In the first 60 min of the adsorption reaction, the phosphates adsorption rate increased, and phosphorus adsorption quantity largely increased. At the 90-min adsorption time, the adsorption rate slowed down, but the adsorbed content of phosphorus increased and sorption has not achieved equilibrium. After 3 h of adsorption time, the phosphorus adsorption content of modified clinoptilolite reached the adsorption equilibrium, and the dynamic adsorption equilibrium process began. In the modified clinoptilolite adsorption experiments of ammonia-nitrogen, the ammonia-nitrogen concentration in the effluent was lower than 1.0 mg/L after 90 min. In addition, the ammonia-nitrogen content of modified clinoptilolite reached close to the adsorption equilibrium of 2.70 mg/g after 150 min.

**Table 3**

Regression parameters of modified clinoptilolite on nitrogen and phosphorus adsorption kinetics.

	Power function adsorption kinetics equations ( $q = at^b$ )			Elovich adsorption kinetics equations ( $q = a + b \ln t$ )		
	$a$	$b$	$R^2$	$a$	$b$	$R^2$
Phosphorus	0.232	0.115	0.968	0.234	0.023	0.982
Ammonia-nitrogen	0.900	0.234	0.889	0.926	0.144	0.969

Meanwhile, regressions of the experimental results were conducted. The adsorption power function and Elovich adsorption kinetics equations are shown in formulae (3)–(6).

Power function adsorption kinetics equations of phosphorus:

$$q = 0.232t^{0.115} \quad (3)$$

Elovich adsorption kinetics equations of phosphorus:

$$q = 0.023 \ln(t) + 0.234 \quad (4)$$

Power function adsorption kinetics equations of ammonia-nitrogen:

$$q = 0.900t^{0.213} \quad (5)$$

Elovich adsorption kinetics equations of ammonia-nitrogen:

$$q = 0.144 \ln(t) + 0.926 \quad (6)$$

The regression parameters and correlation coefficient ( $R^2$ ) in modified clinoptilolite phosphorus adsorption kinetics equations are shown in Table 3.

Based on the  $R^2$  of the adsorption power function and Elovich adsorption kinetics, the Elovich adsorption kinetics equation is better than the adsorption power function in depicting the modified clinoptilolite adsorption kinetics of ammonia-nitrogen and phosphorus [13,14]. Based on the Elovich adsorption kinetics equation, the ammonia-nitrogen and phosphorus removal process of the modified clinoptilolite in water sample is chemisorption.

#### 3.4. Adsorption thermodynamics of modified clinoptilolite sorbing ammonia-nitrogen and phosphates

Studies on adsorption thermodynamics achieved the regular trend, intensity, and driving force in the adsorption process. Therefore, calculating the adsorption experiment results by the variations of standard thermodynamic functions is a vital part in adsorption thermodynamics. The relationship between thermodynamic functions  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ , and equilibrium adsorption distribution coefficient  $K_d$  are shown in Eqs. (7)–(9).

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

$$\Delta G = -RT \ln K_d \quad (9)$$

The equilibrium adsorption distribution coefficient  $K_d$  could be calculated using formulae (10)–(13).

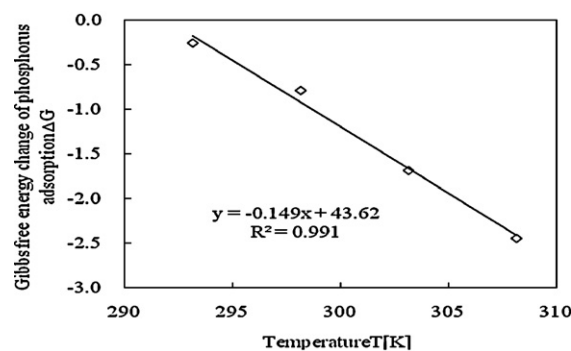
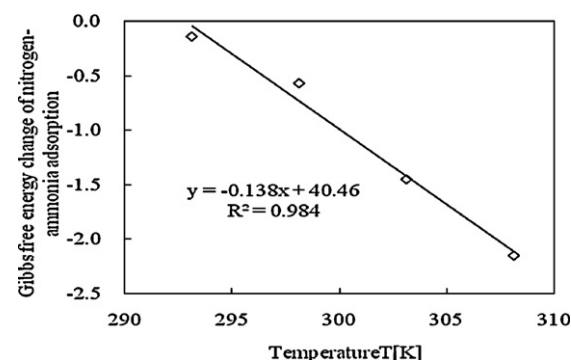
$$\varepsilon = \frac{100K_d}{K_d + (V/m)} \quad (10)$$

$$K_d = \frac{\varepsilon}{1 - \varepsilon} \times \frac{V}{m} \quad (11)$$

$$\varepsilon = \frac{C_0 - C_t}{C_0} \quad (12)$$

$$K_d = \frac{C_0 - C_t}{C_t} \times \frac{V}{m} \quad (13)$$

where  $K_d$  is the equilibrium adsorption distribution coefficient,  $\Delta G$  is the standard free energy of adsorption,  $\Delta H$  is the standard adsorption enthalpy,  $\Delta S$  is the standard adsorption entropy change,

**Fig. 10.** Gibbs function of phosphates adsorption.**Fig. 11.** Gibbs function of ammonia-nitrogen adsorption.**Table 4**

Phosphorus adsorption distribution coefficients and thermodynamic functions of modified clinoptilolite.

$T$ (K)	$K_d$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/K)
293.15	1.11	-0.25	–	–
298.15	1.37	-0.79	43.62	149.4
303.15	1.95	-1.69	–	–
308.15	2.60	-2.44	–	–

**Table 5**

Ammonia-nitrogen adsorption distribution coefficients and thermodynamic functions of modified clinoptilolite.

$T$ (K)	$K_d$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/K)
293.15	1.06	-0.14	–	–
298.15	1.26	-0.57	40.46	138.2
303.15	1.78	-1.45	–	–
308.15	2.32	-2.15	–	–

$R$  is the ideal gas constant,  $T$  is the absolute temperature,  $V$  is the solution volume, and  $m$  is adsorbent dosage.

$K_d$  and  $\Delta G$  were calculated based on modified clinoptilolite adsorption thermodynamics experiment results of ammonia-nitrogen and phosphates at different temperatures.  $\Delta G$  variations were plotted in Figs. 10 and 11. Subsequently,  $\Delta H$  and  $\Delta S$  were obtained after plotting the linear regression lines. The results are shown in Tables 4 and 5.



By mapping  $T$  with  $\Delta G$ , phosphates adsorption correlation coefficient  $R^2$  is 0.991, and ammonia-nitrogen adsorption correlation coefficient  $R^2$  is 0.984. This condition means that a significant linear correlation between  $\Delta G$  and  $T$  exists. At  $\Delta G$  below 0, zeolite adsorption of nitrogen and phosphates is considered a spontaneous process.

At the same temperature, the following condition is observed:  $|\Delta G_{\text{NH}_3\text{-N}}| < |\Delta G_{\text{P}}|$ . This condition means that in simultaneous nitrogen and phosphates removal process using modified clinoptilolite, phosphates is adsorbed first compared to nitrogen. However, as temperature rises,  $\Delta G$  is decreases. This condition means that modified clinoptilolite adsorption of nitrogen and phosphates is better at higher temperatures. A  $\Delta H$  is greater than 0 shows that zeolite adsorption of ammonia-nitrogen and phosphates are an endothermic process. In addition, if  $\Delta S$  is greater than 0 in the adsorption process, ammonia-nitrogen and phosphates tend to be adsorbed on the surface of the zeolite. Generally, with gas molecules adsorbed in the surface of the solid, the entropy goes down [15,16]. The reason being, when gas molecules turn from chaotic gas state to neatly arranged state in the surface of solid adsorbent, the gas molecules degree of freedom is decreases. However, irregular solid surface adsorption in complex solutions is different. In solid–liquid adsorption system, solute adsorption process and solvent desorbing process works simultaneously. In the solute adsorption process, the solute molecule degree of freedom drops and entropy is reduced. Consequently, zeolite adsorption of nitrogen and phosphates is a complex process. On the other hand, entropy increases in the ion exchange process when the exchanged ions from the surface of zeolite return to the solution. Furthermore, the entropy of the whole system will increase when the entropy increase by the ion exchange process is bigger than the entropy decrease by the solute adsorption process. Therefore, entropy effect is the driving force of adsorption process.

#### 4. Conclusions

The modified clinoptilolite obtained by NaCl-, FeCl<sub>3</sub>- and thermal modification has efficient sorption performance and high simultaneous removal effects of ammonia-nitrogen and phosphates. The sorption mechanism of the modified clinoptilolite was revealed by some testing means. The SEM and EDS analysis show that the surface of modified clinoptilolite was dispersed and the specific surface area increased; the contents of Na and Fe increased and the contents of Ca and Mg decreased. The ammonia-nitrogen and phosphate data could be well fitted by the Langmuir isotherm model and the sorption of the modified clinoptilolite to nitrogen and phosphates process involves rapid adsorption and slow

equilibrium. The nitrogen and phosphates adsorption thermodynamics experiments show that the nitrogen and phosphates removal process by modified clinoptilolite is a spontaneous and heat adsorbing process. Lastly, entropy effect is found to be the main driving force.

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