

# Ion-exchange Capability for Ammonium Removal using Zeolite Modified by Potassium Permanganate

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In this study, the ability to remove ammonium aqueous solutions of the natural zeolite particles produced in Jinzhou, Liaoning and the zeolite particles modified by potassium permanganate were characterized by using the static adsorption experiments. The results showed that ammonia adsorption capacity of natural zeolite is preferable, and adsorption capacity of the zeolite particles modified by potassium permanganate is slightly lower, but still maintain preferential adsorption. In addition, the Freundlich isotherm model proved a better fit in the description of ammonia adsorption process than Langmuir model both for the natural zeolites and zeolite particles after potassium permanganate treatment, with  $R^2$  ranging from 0.9328 to 0.9893. The adsorption kinetic data of ammonium onto the zeolite particles modified by potassium permanganate could be well described by a pseudo-second-order kinetics equation.

## 1. Introduction

The water environment quality is deteriorating, and ammonia nitrogen pollution has become the major pollution factors of water plant and sewage treatment plants in China, with the increase in emissions of pollutants. In water supply works, ammonia under the action of microorganisms can be converted to nitrite nitrogen, will be combined with the production of carcinogenic nitrosamines with proteins, a great threat to human health. It's required to strengthen the traditional water purification process for ammonia removes in micro-polluted water. In the drainage projects, many of the sewage treatment plant have to mention the subject of facing the implementation of more stringent standards, because of the more serious water pollution. It's also need to enhance the removal of ammonia nitrogen. Effective method for removing ammonia nitrogen is of great significance.

Conventional ammonia removal methods include physical chemistry, chemical, biological method, all of which are difficult to remove the solubility of ammonia nitrogen effectively. Traditional biological process requires strict control of temperature, pH and other factors, which makes it is of low efficiency with high operating costs. Ion exchange adsorption denitrification by adsorbent such as zeolite is under the spotlight in recent years. Zeolite has a special ion exchange properties, the exchange may occur in the environment of ammonium ion. A large number of studies have shown that natural zeolite has good ammonia removal, while some research about factors such as acid, alkali, salt, temperature, microwave affecting on zeolite adsorption effectiveness of ammonia were carried out. But rare studies focus on the impact of potassium permanganate, a strong oxidant commonly used in water treatment, on the ammonium adsorption performance by zeolite.

In this regards, the following objectives were in this study: (1) denitrification properties of natural zeolite; (2) determination of the effect of potassium permanganate on ammonia removal by natural zeolite; (3) identification of an empirical model that best describes this ion-exchange process. Water purification experiments to provide a reference for the combination of process selection. The result provides a reference for the selection of combination process about water purification.

## 2. Materials and methods

### 2.1 Materials and reagents

The natural zeolite used in this study, which was crushed to a particle size of 0.5~1.5mm originated from Liaoning province, China. The ammonium ion exchange capacity was of 30~50g/kg. The zeolite had the

following main chemical composition(in%): SiO<sub>2</sub>=73, Al<sub>2</sub>O<sub>3</sub>=16. It was washed in deionized water to remove impurities, and was heated at 105°C for drying.

A certain amount of natural zeolite particles weighed was immersed in a certain concentration of potassium permanganate solution for several hours, at solid-liquid ratio of 1:30, and then filtered, washed, dried, to obtain the zeolite particles after potassium permanganate treatment.

Main chemical reagents: Potassium chloride, sodium tartrate, potassium iodide, mercury, sodium hydroxide and hydrochloric acid, etc., all of which were of analytical grade.

## 2.2 Experimental equipment and test method

The main experimental equipment are: electric mixer, SHA-B oscillator, spectrophotometer, electronic balance. The Nessler's reagent colorimetric method was used for the determination of ammonium.

## 2.3 Experimental method

This study was directed to provide emergency alternative technologies for excessive ammonia water, and in the consideration for the reuse possibility of urban sewage treatment plant effluent.

Ammonia in micro-polluted surface water does not exceed 10 mg/L in most instances, and is generally not more than 20 mg/L in secondary biological treatment effluent of municipal sewage treatment plant. Therefore, experimental ammonia concentration in solution is 2~20mg/L. The initial experimental ammonia solution was made of ammonium chloride solved in tap concentration of 1000mg/L, which was diluted to several concentrations gradient for using.

### 2.3.1 The effect of potassium permanganate on the ammonia adsorption capacity of zeolite

In this procedure, the ammonia adsorption capacity of natural zeolite and modified zeolite was investigated with the same dosing quantity in 10mg/L of ammonia solution. The removal procedure, using modified zeolite as an example, was as follow. Take 10mg/L of ammonia solution per 50ml into five bottles of 250ml Erlenmeyer flasks. Add 0.10g, 0.20g, 0.3g, 0.4g, 0.5g modified zeolite by potassium permanganate respectively. Shake them in oscillator at 25±1°C for 24h to achieve adsorption equilibrium. Then after filtering, determine the ammonia nitrogen concentration of the solution. The ammonia exchanged on zeolite was calculated using the equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Where  $q_e$  is the ammonia exchanged on zeolite (mg/g),  $C_0$  and  $C_e$  are the initial and equilibrium concentration of ammonia in solution (mg/L), respectively,  $m$  is the clinoptilolite mass, and  $V$  is the volume of the solution (L).

### 2.3.2 Isothermal absorption

Taking modified zeolite for example, the isothermal absorption procedure was as follow. Take 2mg/L, 4mg/L, 6mg/L, 8mg/L, 10mg/L, 15mg/L, 20mg/L of ammonia solution per 50ml into seven bottles of 250ml Erlenmeyer flasks. Add 0.3g modified zeolite respectively. Shake them in oscillator at 25±1°C for 24h to achieve adsorption equilibrium. Then determine the ammonia nitrogen concentration of the solution after filtering.

### 2.3.3 Ammonia absorption kinetics

Take 10mg/L of ammonia nitrogen concentration solution in 1000ml, and divide into fifteen bottles of 1000ml beakers, and put 2g modified zeolite respectively. Use rapid magnetic stirring to stir for 5min, 10min, 15min, 20min, 25min, 30min, 40min, 60min, 120min, 180min, 240min, 300min, 360min, 480min, and 560min. Take supernatant fluid after filtering, and test the static absorption of ammonia nitrogen concentration in the solution afterwards.

## 3. Results and discussion

### 3.1 Effect of potassium permanganate

Under different dosing quantities, natural zeolite and modified zeolite absorption of ammonia nitrogen is shown in Figure 1.

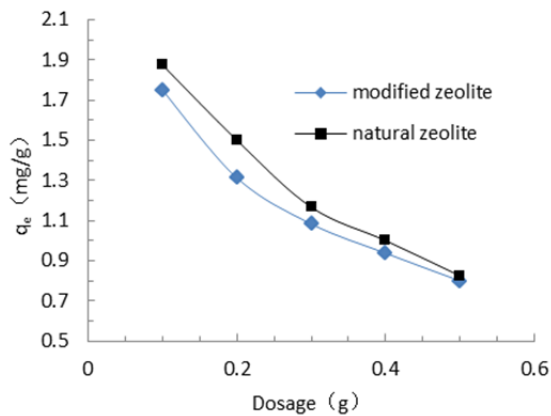


Figure 1: Adsorption of  $\text{NH}_4^+$  by natural zeolite and modified zeolite under different dosing quantities

The ammonia adsorption capacity of modified zeolite is lower than of natural zeolite under different dosing quantities at the same initial  $\text{NH}_4^+$  concentrations. Ammonia nitrogen adsorption capacity of modified zeolite decreased, which may be related to changes in the zeolite surface pore condition. Zeolites are a class of hydrated aluminum silicate minerals with porous skeletal structure, which ion exchange properties closely associated with cavities and channel conditions. This may related to pore clogging because of manganese dioxide reduced from potassium permanganate when the adsorption of ammonia nitrogen produced from simulated wastewater containing a small amount of reducing material, with modified zeolite particles.

The amounts of ammonium removed by natural and modified zeolite were determined. As the dosage of zeolite increased, the removal efficiency of ammonia increased, but the amounts of ammonia adsorbed by per gram of zeolite decreased, adsorbent efficiency declined. This was because before reaching the saturation concentration, in the same amount and concentration of ammonia nitrogen solutions, the more of zeolite particles dosage, the more units of zeolite absorption potentially decreased.

### 3.2 Absorption isotherms of zeolite particles

The ammonia adsorption isotherms of these two kinds of zeolite particles were shown in Figure 2. The adsorption capacity of ammonia nitrogen of natural zeolite and modified zeolite were both increased with the equilibrium concentration of ammonia nitrogen increased. This was because with increasing concentration, adsorption impetus improved.

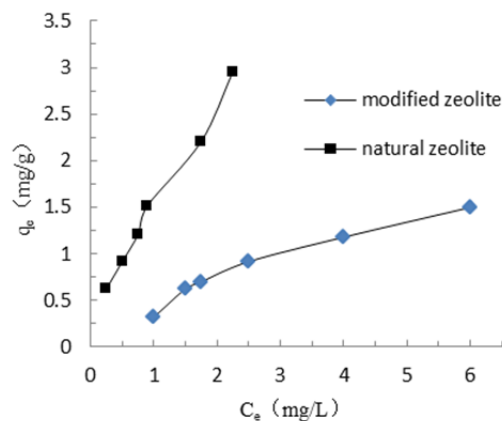


Figure 2:  $\text{NH}_4^+$  adsorption isotherms for natural and modified zeolite particles

To characterize the exchange equilibrium of  $\text{NH}_4^+$  ions by zeolite particles, the Freundlich and Langmuir absorption models were used as follows:

Freundlich equation:

$$q_e = KC_e^{\frac{1}{n}} \quad (2)$$

Where  $q_e$  is the  $\text{NH}_4^+$  exchanged on zeolite (mg/g),  $C_e$  is the initial and equilibrium concentrations of  $\text{NH}_4^+$  (mg/L),  $k$  and  $n$  are constants determined by regression of the experimental isotherm data.

Isotherm converts into:

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \tag{3}$$

Take  $\lg q_e$  as Y factor and  $\lg C_e$  as X factor to make a plane coordinate system. Then make regression of the experimental isotherm data.

Langmuir equation:

$$q_e = \frac{bq^0 C_e}{1 + bC_e} \tag{4}$$

Where  $q^0$  is the maximum adsorption amount on zeolite (mg/g),  $b$  is a constants determined by regression of the experimental isotherm data. The rest parameters are the same as above.

Isotherm converts into:

$$\frac{C_e}{q_e} = \frac{1}{q^0} C_e + \frac{1}{bq^0} \tag{5}$$

Take  $\frac{C_e}{q_e}$  as Y factor and  $C_e$  as X factor to make a plane coordinate system. Then make regression of the experimental isotherm data.

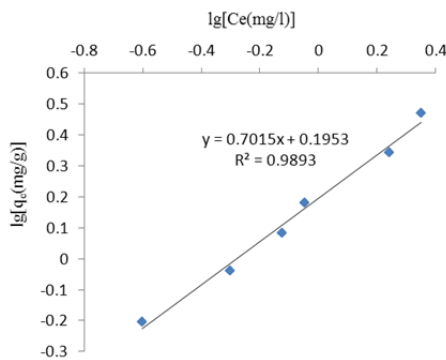


Figure 3: Freundlich adsorption isotherm equation of linear regression of natural zeolite

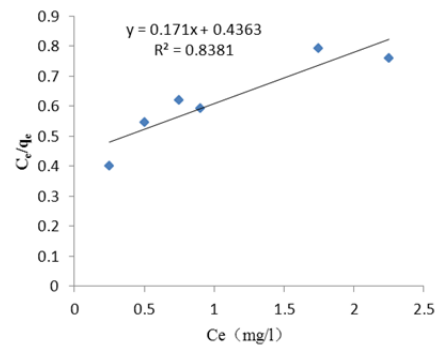


Figure 4: Langmuir adsorption isotherm equation of linear regression of natural zeolite

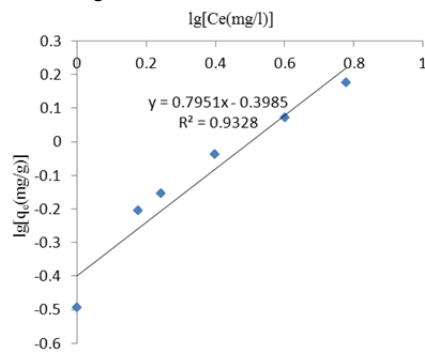


Figure 5: Freundlich adsorption isotherm equation of linear regression of modified zeolite

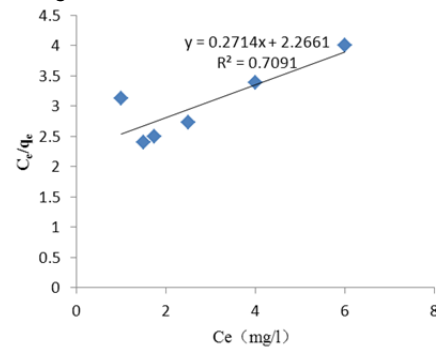


Figure 6: Langmuir adsorption isotherm equation of linear regression of modified zeolite

Fitting parameters of isotherm equation are shown in Tab.1.

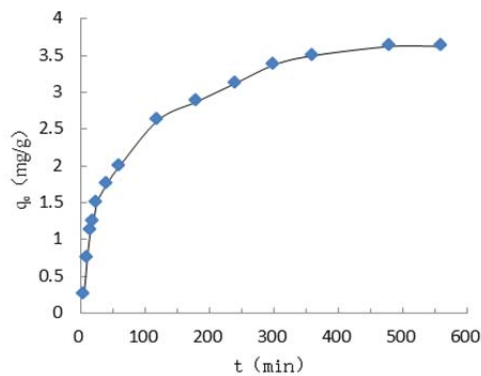
Table 1: Parameters for ammonia nitrogen of natural and modified zeolites adsorption isotherm

Model	Freundlich			Langmuir		
	K	n	R <sup>2</sup>	q <sup>0</sup> (mg/g)	b	R <sup>2</sup>
natural zeolite	1.5678	1.4255	0.9893	5.8480	0.3919	0.8381
modified zeolite	0.3995	1.2577	0.9328	3.6846	0.1198	0.7091

Ion-exchange isotherms characterize the equilibrium relationship between the amounts of exchanged ion by zeolite and its equilibrium concentration in the solution. In this study, the ion-change isotherm data obtained for natural and modified zeolite were fitted to the Freundlich and Langmuir models. The resulting exchange isotherms as well as experimental data are shown in Figure 4 to Figure 6. The estimated model parameters, including R<sup>2</sup>, for the different models are presented in Tab.1, which indicates that the experimental data of NH<sub>4</sub><sup>+</sup> exchange could be well fitted by both two models. It was also made clear that the Freundlich model provided a more consistent fit to the experimental data compared with the Langmuir model. The Freundlich model of natural zeolite which correlation coefficient R<sup>2</sup> is 0.9893, provided a more consistent fit than modified zeolite. Freundlich absorption isotherm parameter n in modified zeolite model is still greater than 1, which means the modified zeolite absorption is also a preferential absorption of ammonia nitrogen. This suggests that the modified zeolite for the algae and algae toxin maintains the effective of ammonia nitrogen removal.

### 3.3 Ammonia absorption kinetics

Kinetic models were employed to describe NH<sub>4</sub><sup>+</sup> adsorption to the modified zeolite. Adsorption kinetics is the study of adsorption speed, and it is closely related to contact time. Under different adsorption times, modified zeolite absorption of ammonia nitrogen is shown in Figure 7.

Figure 7: Kinetic curve of NH<sub>4</sub><sup>+</sup> adsorption for modified zeolite

The adsorption capacity of the zeolite to ammonia nitrogen changed significantly with the adsorption time, the adsorption capacity increased rapidly in the first 40 minutes, then became slower, to 500 minutes reached the basic balance, which is consistent with the equilibrium time of natural zeolite and modified zeolite in literature (Ma, 2000; Zhang, 2010). It indicates that the adsorption rate of modified zeolite does not change obviously. The experimental data were fitted by pseudo-first-order and pseudo-second-order equations to study the adsorption kinetics.

Pseudo -first-order equation:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

Pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where  $q_e$  is the amount of ammonium absorbed at equilibrium, mg/g;  $q_t$  is the amount of ammonium absorbed at time  $t$ , mg/g;  $K_1$  is the pseudo-first-order adsorption rate constant, min<sup>-1</sup>;  $K_2$  is the pseudo-second-order adsorption rate constant, g/(mg·min). R<sup>2</sup> for the different models were determined, and a higher R<sup>2</sup> value was considered to represent goodness of conformity between the measured and estimated NH<sub>4</sub><sup>+</sup> absorbed data. The fitting results are shown in Tab.2. The fitting coefficient of pseudo-second-order equation is higher than that of pseudo-first-order equation, the former is better than the latter to fit the adsorption kinetic characteristics of adsorbed NH<sub>4</sub><sup>+</sup>.

Table 2: Kinetic models for  $\text{NH}_4^+$  adsorb from modified zeolite

$q_{e,\text{exp}}$ (mg/g)	Pseudo -first-order equation			Pseudo-second-order equation		
	$K_1$ ( $\text{min}^{-1}$ )	$q_{e,\text{cal}}$ (mg/g)	$R^2$	$K_2$ ( $\text{g}/(\text{mg}\cdot\text{min})$ )	$q_{e,\text{cal}}$ (mg/g)	$R^2$
3.63	0.11	3.5887	0.9136	0.0048	3.9620	0.9947

#### 4. Conclusions

In this study, the  $\text{NH}_4^+$  ion-exchange capacity of zeolite modified by potassium permanganate decreased slightly than natural zeolite, but it's still a preferential adsorption. Ion exchange data was fitted to the Freundlich, Langmuir models, and the Freundlich model provided a more consistent fit to the experimental data. Kinetic models were employed to describe  $\text{NH}_4^+$  adsorption to the modified zeolite, and pseudo-second-order equation is a suitable model.

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