

## Change and improving of ammonium exchange capacity onto zeolite in seawater

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**Abstract.** The ammonium exchange capacity change of zeolite in seawater and its improving were studied. The different of ammonium exchange of zeolite in water and seawater, the ammonium exchange effect of the  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions were investigated. The methods that HCl and NaCl aqueous solutions soaked the natural zeolites were tried to improve the ammonium exchange capacity of the zeolites in seawater. The results indicated that the ammonium uptake of the zeolites in seawater is less than water, but its speed is quicker, because of the competitive exchange of metal ions in seawater. The exchange equilibrium and kinetics exchange gave a better fit to Freundlich isotherm equation and the pseudo-second-order model, respectively. The effect of the metal ions suggested an order of preference  $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$  for the natural zeolite. The zeolite soaked with HCl solution should modified its pore structure, and soaked with NaCl solutions increased the Na content of the zeolite, which led to ammonium exchange capacities of the zeolite improve.

**Keywords:** ammonium, zeolite, seawater, ion exchange.

### 1. Introduction

With rapid economic development and urban intensification, a large quantity of ammonium containing wastewater was discharged into the ocean and caused algal blooms. In China, 0.6 million tons of ammonium ( $\text{NH}_3\text{-N}$ ) were discharged into the ocean, the red tides occurred 69 times and 10892  $\text{km}^2$  in 2010 [1]. It made great harm to the fish and other aquatic organism. Moreover, seaculture is distributed from south to north along the coast in China. The accumulation of fish dung makes the ammonium increasing dramatically on seaculture. It will make some rare fishes and aquatic organisms to die and cause great economic losses. Thus, the study of remove ammonium from seawater is urgency and importance.

Most ways of ammonium removal need to replace the water or treat twice, so they are inappropriate for use in seaculture. Adsorption/ion exchange method [2] avoids changing the water and will extend the use time of water. The reaction process is stable, easy to be controlled. And the renewable exchanger makes the processing cost less. It is the best way to remove the ammonium of seaculture. Natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina- and silica tetrahedra which result in an open and stable three-dimensional honeycomb structure [3] possessing high exchange capacity, selectivity, higher void volume, and great affinity for ammonium [4]. It is a good exchanger to remove ammonium from seawater due to its wide distribution, low cost, relative simplicity of application [5].

Presently, a large number of studies related to the removal of ammonium from aqueous solution using different zeolites have been reported [6-8]. Although zeolite generally exhibits a high selectivity for ammonium, there are some uncertainty on the selectivity differences between potassium, Sodium, calcium and magnesium. Farkaš provided an order of preference  $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$  [9], whereas Hankins et al suggested  $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+}$  [10]. It seems that natural zeolites from various places have different

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characters, so it is need to be sure. These most studies researched ammonium exchange performance and improvement of zeolite in water, and rarely involve seawater. Therefore, the object of this research is to investigate the ammonium exchange capacity change of zeolite in seawater and its improving. It compared the ammonium uptake of zeolite in seawater to water. The effect of the individual presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ion, which always coexist with ammonium in seawater, upon ammonium uptake of zeolite was also investigated. The ammonium exchange capacity of the modified zeolite was experimented in seawater.

## 2. Materials and Methods

### 2.1. Materials

The natural zeolite sample originated from Dalian city (China). The analysis of the chemical properties of the zeolite provided by the manufacturer is shown in Table 1. The zeolite was crushed and classified to a size range of 0.45-0.9 mm. The fragments were washed with deionized water to remove water-soluble residues and dried in an oven at 100 °C for 1 h. According to the major ion concentration of the 35 ‰ salinity seawater (the world average salinity of seawater) [11], the simulated seawater was prepared with NaCl,  $\text{MgCl}_2$ , KCl,  $\text{CaCl}_2$  and the deionized water. The  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  ion concentration was 10.5g/L, 1.35g/L, 0.38g/L and 0.4g/L, respectively. Then dried  $\text{NH}_4\text{Cl}$  was added to it for 1000mg/L ammonium stock solution.

Table 1. Chemical composition of the natural zeolite (wt%)

Constituent	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	$\text{TiO}_2$	MnO	MgO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	Loss on ignition
Value (%)	70.62	12.43	1.85	2.68	0.18	0.08	0.87	0.33	1.03	0.04	9.89

### 2.2. Procedure for the modification of zeolite

Samples of the natural zeolite were soaked in 1 M HCl, 1 M NaCl solution at 30 °C or 98 °C for 2 h, respectively. These zeolite samples were then washed four times with deionized water and dried in an oven at 100 °C for 1 h. The contents of various elements in the different zeolite samples were measured by atomic absorption spectroscopy using a PE3100 spectrometer. The structural parameters of the different zeolites were determined by low-temperature (77.7 K) nitrogen adsorption/desorption. The adsorption data, obtained on an ASAP 2010 apparatus, allowed the BET surface area ( $S_{\text{BET}}$ ), the total porous volume ( $V_p$ ), and the average pore diameter ( $D_p$ ) to be calculated.

### 2.3. Experimental details for measuring the ammonium exchange of zeolite

#### 2.3.1 Kinetic study

0.5 g samples of zeolite were added to 50 mL aliquots of 200 mg/L  $\text{NH}_4\text{Cl}$  water solutions. The respective mixtures were shaken at a rate of 100 r/s at 35 °C. After supernatant was obtained from it, NaOH was added to precipitate the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions of the seawater. The two phases were separated by filtration through a 0.2  $\mu\text{m}$  microporous membrane filter after different time intervals (0.5-6 h). The ammonium concentrations in the aqueous phase were analyzed by a colorimetric method using Nessler's solution [12].

#### 2.3.2 Metal ions effect study

To study the effect of metal ions in seawater, 50 mL aliquots of 200 mg/L  $\text{NH}_4\text{Cl}$  solution were adjusted with different concentration metal ions and then equilibrated with 0.5 g portions of zeolite. After shaking for 24 h, the supernatant was obtained from it. The final ammonium concentration remaining in the aqueous phase was analyzed in the same way as described above.

#### 2.3.3 Equilibrium study

0.5 g samples of zeolite were added to 50 mL aliquots of  $\text{NH}_4\text{Cl}$  simulated seawater solutions with different concentrations (0-340 mg/L) and the respective mixtures were shaken at a rate of 100 r/s at 35 °C. After 24 h, the supernatant was obtained from it. The ammonium concentration in the liquid phase was analyzed in the same way as described above. This approach was adopted to test the different modified zeolites.

### 3. Results and Discussion

#### 3.1. Ammonium-exchange of zeolite in different water

Fig. 1 shows the ammonium uptake of zeolite in seawater was less than in water obviously, because of the competitive exchange of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  in seawater. To characterize the exchange equilibrium of ammonium in the different waters, the Langmuir and Freundlich models were used and are as equation (1)-(2), respectively.

$$\text{Langmuir} \quad \frac{C_i}{q_i} = \frac{1}{q_m} \cdot C_i + \frac{1}{q_m K_L} \quad (1) \quad \text{Freundlich} \quad \log q_i = \log k_f + \frac{1}{n} \log C_i \quad (2)$$

where  $q_i$  (mg/g) and  $C_i$  (mg/L) are the amount of ammonium exchanged by per unit mass of zeolite at equilibrium and the ammonium concentration in the solution at equilibrium, respectively. and  $q_m$  (mg/g) and  $k_L$  (L/mg) are the maximum exchange capacity of the zeolite and the Langmuir constant, respectively.  $k_f$  (mg/g) is the Freundlich constant indicating the exchange capacity of the exchanger. and  $1/n$  is an empirical parameter related to the intensity of exchange, which varies with the heterogeneity of the material.

After fitting the experimental data with Eq. (1) - (2), it was found that the Freundlich model yielded a much better fitting ( $R^2 = 0.999-0.995$ ) of the data compared with the Langmuir model ( $R^2 = 0.894-0.936$ ). In addition, the magnitude of the constant  $1/n$  for the Freundlich isotherm is a measure of the exchange intensity or surface heterogeneity and ranges between 0 and 1. In this study, the values of  $1/n$  for different water were smaller than 1, which indicated that the exchange conditions were favorable [13].

#### 3.2. Ammonium-exchange speed of zeolite in different water

The ammonium-exchange kinetic curve of zeolite is shown in Fig. 2. Ammonium exchange speed of zeolite in the seawater was quicker than in fresh water. There were  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  and so on metal ions in seawater, when ammonium was exchange with zeolite. These metal ions reacted with zeolite, but some were replaced by  $\text{NH}_4^+$  ions immediately. It increased exchange speed relatively rapidly to fresh water. And some active sites of zeolite, which could be exchanged, had not been re-replacement of  $\text{NH}_4^+$  ions, so that the final ammonium uptake of zeolite in seawater was less than the amount in fresh water.

In order to determine the rate-controlling step of the process and to evaluate the diffusion coefficients, a pseudo-second-order model [14], Vermeulen's model [15], and the film diffusion control model [16] were used to study the ammonium exchange kinetics of zeolite and are expressed as equation (3)-(5), respectively.

$$\text{Pseudo-second-order} \quad \frac{t}{q_i} = \frac{1}{K_2 q_m^2} + \frac{1}{q_m} \quad (3) \quad \text{Vermeulen's} \quad -\ln(1-U(t)^2) = t \left( \frac{D_p \pi^2}{r^2} \right) \quad (4)$$

$$\text{Film diffusion control} \quad -\ln(1-U(t)) = t \left( \frac{3D_f C}{r_p \delta C_m} \right) \quad (5)$$

where  $k_2$  (g/(h·mg)) is the rate constant of the pseudo-second-order model, and  $q_t$  (mg/g) and  $q_m$  (mg/g) are the amounts of ammonium exchanged on the zeolite at time  $t$  and equilibrium.  $U(t)$  is defined as the ratio between the mass of ammonium exchanged at a certain time  $t$  and the maximum amount of ammonium exchanged.  $D_p$  ( $\text{m}^2/\text{s}$ ) is the diffusion coefficient in the exchanger, and  $r$  (m) is the radius of the particle.  $D_f$  is the diffusion coefficient in the film ( $\text{m}^2/\text{s}$ ).  $C$  and  $C_m$  ammonium concentrations in the solution and in the exchanger, respectively ( $\text{mol}/\text{m}^3$ ).  $\delta$  is the film thickness accepted as  $10^{-4}$  cm for poorly stirred solution.

The experimental data shown in Fig. 2 were fitted to Eqs. (3)–(5). The correlation coefficients and criteria parameters for the different kinetic models were calculated and. A high correlation coefficient ( $R^2 = 0.997-0.999$ ) was obtained by the pseudo-second-order kinetic model (Vermeulen's model correlation coefficient ( $R^2 = 0.930-0.997$ ) and the film diffusion control model correlation coefficient ( $R^2 = 0.897-0.993$ )). Thus, the pseudo-second-order kinetic model approximation gave a better correlation for all of the data compared to the other two models.

#### 3.3. Metal ions effect of ammonium exchange of zeolite

The experimental results obtained for ammonium removal by natural zeolite in the individual presence of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions are shown in Fig. 3, which reveal that there is a significant ammonium uptake

reduction of zeolite in the presence of other metal ions. As shown in Fig. 3, when the concentrations of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$  and  $Na^+$  increased from 0 to 2 g/L, the uptake of ammonium decreased from 11.8 to 10.1, 9.2, 9.0, and 5.3 mg/g, respectively. When  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  or  $Mg^{2+}$  was presented in the solution, the uptake of ammonium decreased due to the competition caused by the other cations. The competitive effect was greatest for  $K^+$ , followed by  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  at the same equivalent cation concentration. It indicated that the selectivity order of ammonium over other cations on the zeolite was  $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ . Similar results were reported by Ame et al [17, 18]. Although the  $K^+$  ions affected the ammonium exchange mostly, but  $Na^+$  ion content in seawater is the maximum and it has the greatest affect to ammonium exchange.

### 3.4. Ammonium exchange of different modified zeolite in seawater

From Figure 4, the ammonium uptakes of zeolites were soaked with HCl or NaCl have greatly improved in seawater. The pore structure and metal content of the different zeolites were obtained in Table 2. The

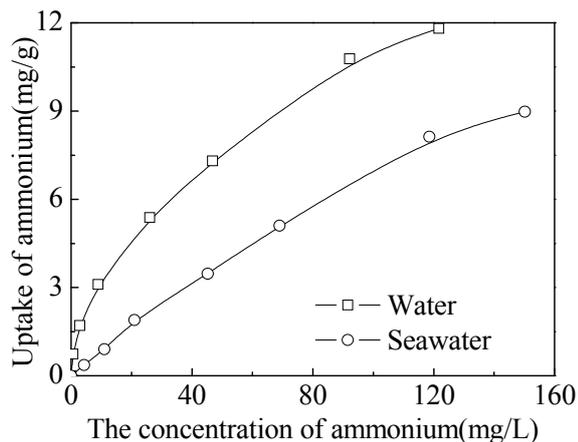


Figure 1. Ammonium-exchange isotherms (35 °C) of zeolite in different water (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 0-400 mg/L; contact time, 24 h).

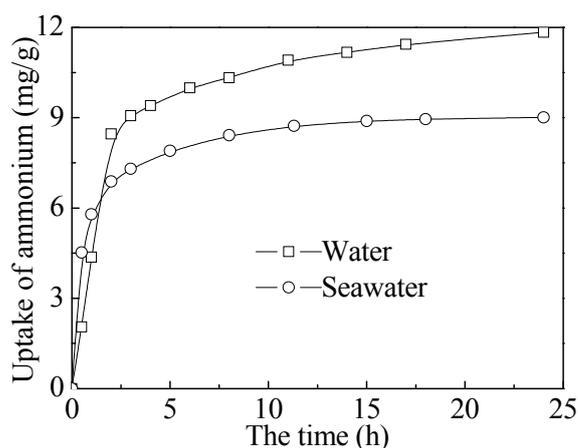


Figure 2. Kinetic curve of ammonium exchange in different water (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 200 mg/L; time intervals, 0.5-6 h).

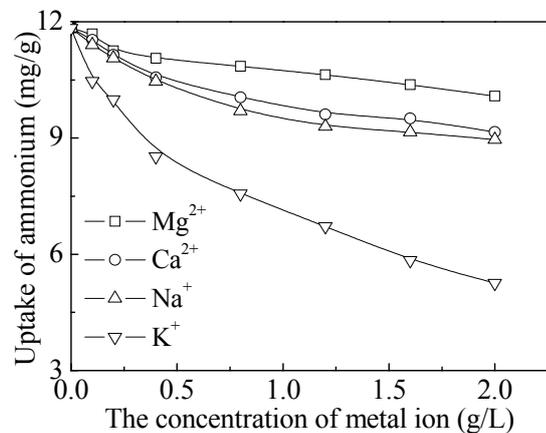


Figure 3. Effect of the different metal ion on ammonium exchange of zeolite (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 200 mg/L; contact time, 24 h).

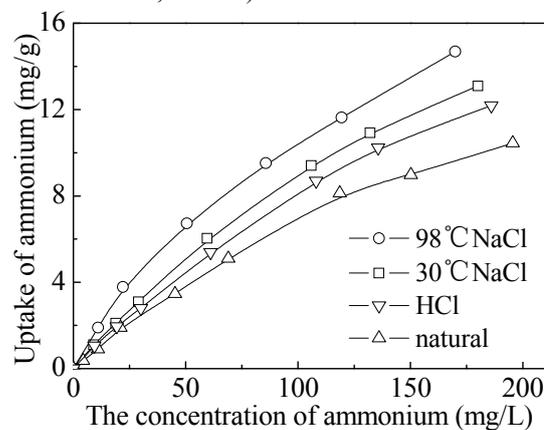


Figure 4. Ammonium-exchange isotherms (35 °C) of zeolite samples modified using different methods in seawater (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 0-400 mg/L; contact time, 24 h).

Table 2. Porous structure parameters (at P/P0 = 0.98) and K, Na, Ca, Mg contents of zeolites modified by different modification methods.

Modification methods	BET surface area (m <sup>2</sup> /g)	Total porous volume (cm <sup>3</sup> /g)	Average pore diameter (Å)	K (%)	Na (%)	Ca (%)	Mg (%)
Original	16.1995	0.037234	91.9381	0.85	0.24	1.91	0.52
HCl soak	16.4827	0.049030	110.1192	0.72	0.23	1.37	0.36
30°C NaCl soak	16.2241	0.037613	94.8382	0.85	0.71	1.54	0.47
98°C NaCl soak	16.0762	0.036815	96.0128	0.81	1.63	08	0.26

method of HCl soaking zeolite will reduce the exchangeable metal elements of the zeolite, but its BET surface area and average pore diameter increase, which led to an increase of ammonium adsorption exchange capacities of the zeolite. What's more, the ammonium exchange capacity of the zeolite soaked with NaCl increased obviously. The pore structure of the NaCl modified zeolite changed little, but its Na content increased, especially soaking at 98°C (see Table 2), which led to its ion exchange capacities increase. Both HCl and NaCl soaking method improved the exchange capacity of zeolite effectively.

#### 4. Conclusion

The ammonium uptake of zeolite in seawater was less than fresh water, because of the competitive exchange of metal ions in seawater. The equilibrium curve fitted to Freundlich isotherm equation better. The ammonium exchange speed was quicker than in fresh water and the ammonium-exchange kinetic curve were described with the pseudo-second-order kinetic model. The effect of the major metal ions of seawater on the ammonium uptake followed the order of preference  $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ . The methods of HCl and NaCl soaking zeolite modified pore structure and increased the Na content of the zeolite, respectively, which led to the ammonium exchange capacity of the zeolites improve obviously.

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