

Removal of Ammonium from Aqueous Solution Using Natural and Modified Dalian Clinoptilolite

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The removal of ammonium from aqueous media using Chinese Dalian clinoptilolite has been investigated. To improve the ammonium exchange of the clinoptilolite, its modifications in aqueous NaCl solution at different temperatures and under different power levels of ultrasonication have been tested. The ammonium-exchange isotherms of the clinoptilolite have been determined. The effects of solution pH and the different modifications of the clinoptilolite on ammonium exchange have been further studied. The results showed that a pseudo-second-order model gave a better correlation for all of the kinetic data as compared to Vermeulen's model or an intraparticle diffusion model. The optimal pH of solutions for ammonium exchange with clinoptilolite has been identified to be between 3 and 9. Natural clinoptilolite soaked in aqueous NaCl solution at 98 °C had the highest sodium content, leading to an improved ammonium-exchange capacity. The ammonium-exchange capacity of clinoptilolite could be improved by increasing the temperature at which it was soaked in aqueous NaCl solution, but it could not be improved by increasing the power level of ultrasonication continuously. All of the ammonium-exchange equilibrium isotherms, with both natural and modified clinoptilolite, conformed well to the Freundlich model.

Key Words: Modified clinoptilolite, Ammonium, Exchange, Aqueous solution.

INTRODUCTION

Water is fundamental importance for life on Earth. About 2.66 % of the total global water resources are fresh water, although their pollution is a serious issue. In China, 1.2 million tons of ammonium (NH₃-N) were discharged into water in 2010¹. The removal of ammonium from wastewater has attracted much attention due to its extreme toxicity to most fish species, as well as eutrophication in rivers, estuaries, lakes and in general, superficial reservoirs².

The traditional methods for ammonium removal from municipal and industrial wastewaters include air stripping, biological nitrification-denitrification and adsorption/ion-exchange. However, air stripping can easily lead to recontamination^{3,4}, while biological nitrification-denitrification does not respond well to shock loads of ammonium, such that unacceptable peaks may appear in the effluent ammonium concentration^{5,6}. Compared to these two methods, the adsorption/ion-exchange method takes up relatively less space and can maintain high ammonium removing efficiency at low temperatures, making its application and operation relatively simple^{7,8}. Thus, it is widely regarded as the best choice of ammonium removal and researched by many scholars.

The need of an adsorption/ion-exchange method is the ammonium exchange of the adsorbent/ion-exchanger^{9,10}. A common adsorbent/ion-exchanger with a high affinity for ammonium is clinoptilolite, a naturally occurring zeolite. Clinoptilolite has been reported to have a classical aluminosilicate cage-like structure and therefore exhibits significant macroporosity. It appears to be advantageous over some conventional and expensive adsorbent/ion-exchangers for the removal of high concentrations of ammonium from wastewater^{11,12}. Clinoptilolite tuffs have been studied for the removal of ammonium from aqueous solutions, including material from Poland¹³, Brazil¹⁴, Turkey¹⁵, Sweden¹⁶, Bulgaria¹⁷ and Lithuania¹⁸. Leyva-Ramos *et al.*¹⁹ and Wen *et al.*²⁰ modified the natural chabazite and zeolite with NaCl solution and made their ammonium exchange capacity improve. Lecheng *et al.*²¹ treated the zeolite with NaCl solution under microwave irradiation and got higher ammonium exchange capacity too. But microwave equipment costs more, so this paper tried to modified the clinoptilolite with NaCl solution on the condition of ultrasonication or heating and tested their ammonium exchange capacity. In addition, due to the different clinoptilolite materials have their particular characteristics, the effects of solution pH for ammonium exchange, the kinetic and equilibrium isotherms of the ammonium exchange on clinoptilolites have been further studied.

TABLE-1
CHEMICAL COMPOSITION OF THE NATURAL CLINOPTILOLITE (wt %)

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	MnO	MgO	Na ₂ O	K ₂ O	P ₂ 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

EXPERIMENTAL

Samples of the natural clinoptilolite (denoted herein as natural) originated from Dalian city (China). The analysis of the chemical properties of the clinoptilolite provided by the manufacturer is shown in Table-1. The clinoptilolite 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.

Modification of clinoptilolite: Samples of the natural clinoptilolite were soaked in 1 M NaCl solution, then incubated at 30, 50, 80 or 98 °C or subjected to different power levels of ultrasonication for 1 h, respectively. These clinoptilolite 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 clinoptilolite samples were measured by atomic absorption spectroscopy using a PE3100 spectrometer. The structural parameters of the different clinoptilolites 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_{BET}), the total porous volume (V_p) and the average pore diameter (D_p) to be calculated.

Measurement of the ammonium exchange of clinoptilolite

Kinetic study: 0.5 g samples of clinoptilolite were added to 50 mL aliquots of 200 mg/L NH₄Cl solution. The respective mixtures were shaken at a rate of 100 r/s at 35 °C. The two phases were separated by filtration through a 0.2 μm 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 solution²².

pH Effect study: To study the effect of solution pH, 50 mL aliquots of 200 mg/L NH₄Cl solution were adjusted with HCl or NaOH to various pH values and then equilibrated with 0.5 g portions of clinoptilolite. After shaking for 24 h, the two phases were separated by filtration through a 0.2 μm microporous membrane filter. The final ammonia concentration remaining in the aqueous phase was analyzed in the same way as described above. The pH values were monitored periodically throughout the experiment with a pH meter.

Equilibrium study: 0.5 g samples of clinoptilolite were added to 50 mL aliquots of NH₄Cl solutions with different concentrations (0-400 mg/L) and the respective mixtures were shaken at a rate of 100 r/s at 35 °C. After 24 h, the two phases were separated by filtration through a 0.2 μm microporous membrane filter. The ammonia concentration in the liquid phase was analyzed. This approach was adopted to test the different clinoptilolites.

Calculation of the uptake of ammonium: Ammonium uptake (q_t) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where, q_t is the total amount of exchanged ammonium (mg/g), C_0 and C_t are the initial and equilibrium concentrations of ammonium solution (mg/L), respectively, V is the solution volume (L) and M is the weight of adsorbent (g).

RESULTS AND DISCUSSION

Ammonium-exchange kinetics of clinoptilolite: The ammonium-exchange kinetic curve of clinoptilolite is shown in Fig. 1. After 17 h, the exchange rate slowed down and gradually reached equilibrium. In order to determine the rate-controlling step of the process and to evaluate the diffusion coefficients, a pseudo-second-order model, Vermeulen's model and an intraparticle diffusion model were used to study the ammonium-exchange kinetics of clinoptilolite. The kinetic equation of the pseudo-second-order model²³ has the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{t}{q_m} \quad (2)$$

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 clinoptilolite at time t and equilibrium, respectively.

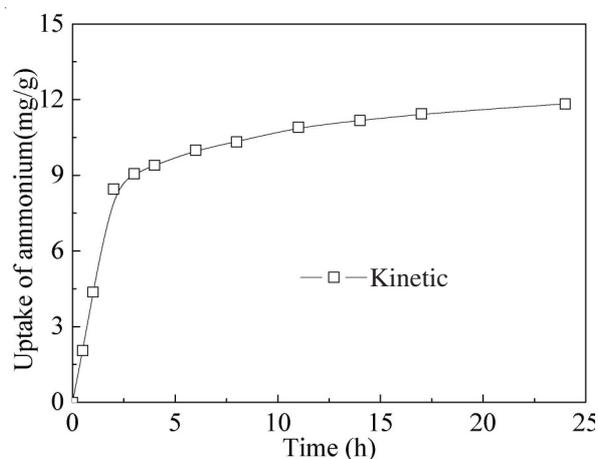


Fig. 1. Kinetic curve of ammonium exchange (T , 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 200 mg/L; time intervals, 0.5-6 h)

Vermeulen's model²⁴ for the fractional attainment of equilibrium is expressed as:

$$-\ln(1 - U(t)^2) = t \left(\frac{D_p \pi^2}{r^2} \right) \quad (3)$$

where, $U(t)$ 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 (m^2/s) is the diffusion coefficient in the adsorbent and r (m) is the radius of the particle.

The intraparticle diffusion model²⁵ is described by the following equation:

$$q_t = k_i t^{1/2} + B \quad (4)$$

where, k_i ($\text{mg}/(\text{h}^{1/2} \text{g})$) is the intra-particle diffusion rate constant, q_t (mg/g) is the amount of ammonium exchanged at time t and B is the intercept.

The experimental data shown in Fig. 1 were fitted to eqns. (2)-(4). The correlation coefficients and criteria parameters for the different kinetic models were calculated and are shown in Table-2. As can be seen from Table-2, a high correlation coefficient ($R^2 = 0.997$) was obtained by the pseudo-second-order kinetic model and the calculated q_m ($12.62 \text{ mg}/\text{g}$) was close to the experimental value at 24 h. Thus, the pseudo-second-order kinetic model approximation gave a better correlation for all of the data compared to the other two models.

Model	R^2	Other parameter
Pseudo-second-order	0.997	$k_2 = 8.241 \times 10^{-3} \text{ g}/(\text{h mg})$ $q_m = 12.62 \text{ mg}/\text{g}$
Vermeulen's	0.956	$D_p = 8.241 \times 10^{-13} \text{ m}^2/\text{s}$
Intraparticle diffusion	0.949	$k_i = 0.1746 \text{ mg}/(\text{h}^{1/2} \text{g})$

Effect of the solution pH on ammonium exchange:

Ammonium in aqueous solution can be found in a dissociating form as ammonium ion, NH_4^+ , or without dissociating as dissolved ammonia, NH_3 . The equilibrium between these two species is dependent upon the solution pH and temperature. It can be represented by the following chemical reaction (eqn. 5).



$$\text{pK}_a = -\lg \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 8.85 \quad (6)$$

At a solution temperature of 35°C , the ammonium dissociation therein may be expressed with an equilibrium constant²⁶ according to eqn. (6). On the basis of eqn. (6), the speciation diagram of ammonium in aqueous solution is drawn in Fig. 2. It may be noted that at $\text{pH} < 7$, the predominant species is the NH_4^+ ion, but at $\text{pH} > 11$, it is dissolved in ammonia.

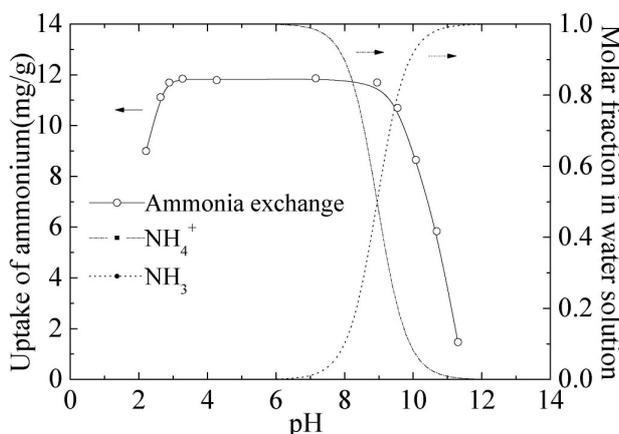


Fig. 2. Dissociation curve of ammonium ($T, 35^\circ\text{C}$) and the ammonium exchange of clinoptilolite at different pH in aqueous solution. ($T, 35^\circ\text{C}$; solid concentration, $10 \text{ g}/\text{L}$; initial ammonium concentration, $200 \text{ mg}/\text{L}$; contact time, 24 h)

The effect of the solution pH on the ammonium exchange of clinoptilolite is shown in Fig. 2. At $\text{pH} < 3$, the ammonium-

exchange capacity of clinoptilolite diminished as the exchange of H^+ ion was predominant in the solution. The uptake of ammonium remained constant between $\text{pH} 3$ and 9 , as the reaction between clinoptilolite and ammonium was mainly ascribed to ion exchange. At $\text{pH} > 9$, the concentration of NH_3 was higher than that of NH_4^+ ions, the exchange of ammonium ions diminished and consequently the uptake of ammonium decreased.

Ammonium exchange of the ultrasonication clinoptilolites: To study the effect on ammonium uptake of modifying the clinoptilolite with NaCl solution, samples of the natural clinoptilolite were soaked in NaCl solution and subjected to different power levels of ultrasonication. Figs. 3 and 4 showed that an appropriate level of ultrasonication served to improve the ammonium-exchange capacity of the clinoptilolite, while too high a power level of ultrasonication had a detrimental effect. From the Table-3, it showed the ultrasonication caused framework collapse and losses of partial clinoptilolite, resulting in pore blockage and the decreases in porous volume and BET surface area. At the same time, ultrasonication radiation enhanced replacement of the metal ions of clinoptilolite by Na^+ ions and made the exchangeable metal such as sodium of clinoptilolite dissolve into solution. The porous structure changes of clinoptilolite were not the determining factors of ammonium exchange capacity changes of clinoptilolite. When the power level of ultrasonication was 140 W , the replacement metal ions of clinoptilolite by Na^+ were more than dissolvable sodium and the sodium contents of clinoptilolite reached the maximum, which led to the ammonium exchange capacity improving (Fig. 4). But the ultrasonication power exceeded 140 W , this effect became the opposite, which lead to the ammonium exchange capacity decreasing.

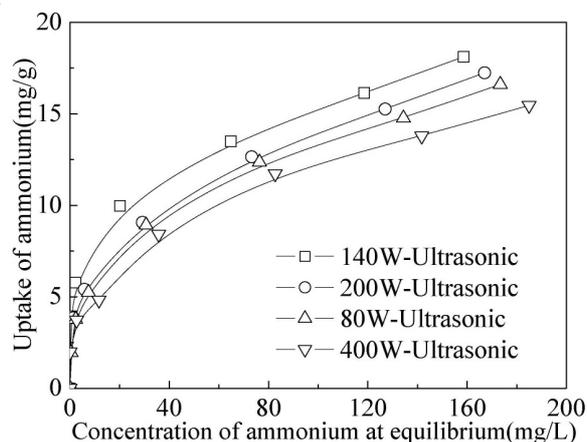


Fig. 3. Ammonium-exchange isotherms of clinoptilolite samples modified with NaCl solutions at different levels of ultrasonication ($T, 35^\circ\text{C}$; solid concentration, $10 \text{ g}/\text{L}$; initial ammonium concentration, $0-400 \text{ mg}/\text{L}$; contact time, 24 h)

Ammonium exchange of the heat treatment clinoptilolites: The ammonium-exchange capacity of the clinoptilolite increased on increasing the temperature at which it was soaked in NaCl solution (Fig. 5). As the temperature was raised, the porous structure of clinoptilolite changed little, but the rate of movement of Na^+ ions in the solution was accelerated and so more Na^+ ions in the free solution replaced metal ions in the

TABLE-3
POROUS STRUCTURE PARAMETERS (at $P/P_0 = 0.98$) and K, Na, Ca, Mg CONTENTS
OF CLINOPTILOLITES MODIFIED BY DIFFERENT MODIFICATION METHODS

Modification methods of clinoptilolite	BET surface area (m^2/g)	Total porous volume (cm^3/g)	Average pore diameter (\AA)	K (%)	Na (%)	Ca (%)	Mg (%)
Original clinoptilolite	16.1995	0.037234	91.9381	0.85	0.24	1.91	0.52
140 W ultrasonic	16.0002	0.034685	114.6872	0.84	0.99	1.38	0.38
400 W ultrasonic	14.8847	0.029130	129.1564	0.79	0.18	1.23	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	0.86	0.26

clinoptilolite owing to the enhanced force of the collisions. When the temperature of the NaCl solution reached 98 °C, the modified clinoptilolite obtained had the highest sodium content (Table-3) and thus attained the best exchange capacity. Comparing the different clinoptilolite modification methods for their capacity in improving ammonium removal, treating clinoptilolite in NaCl solution at 98 °C proved to be the most efficient method, followed by ultrasonication at 140 W; treatment with aqueous NaCl at 30 °C proved to be least effective.

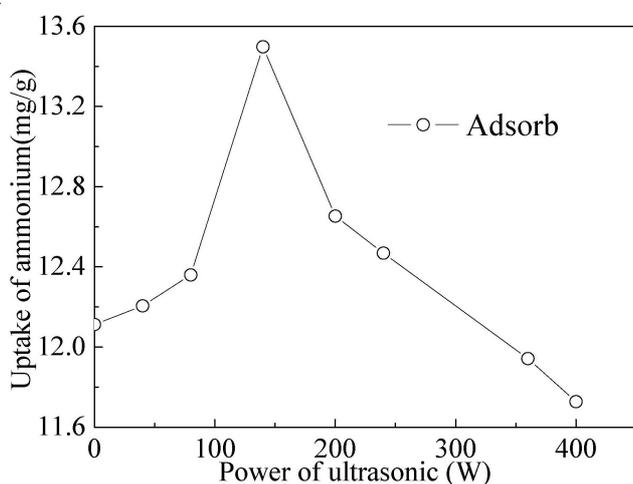


Fig. 4. Effect of different levels of ultrasonication on the ammonium-exchange capacities of clinoptilolite samples (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 200 mg/L; contact time, 24 h)

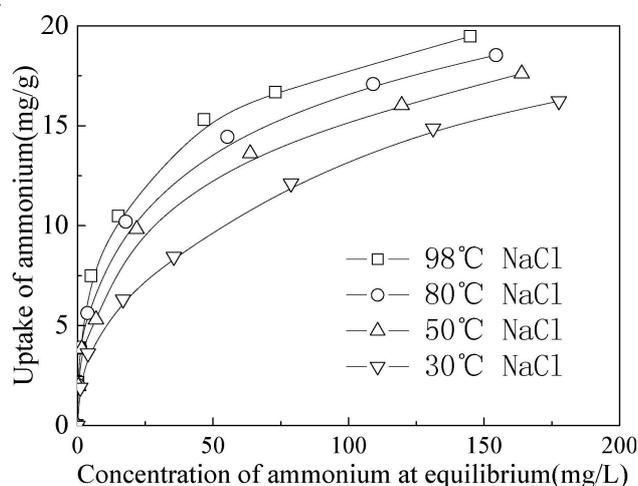


Fig. 5. Ammonium-exchange isotherms (35 °C) of clinoptilolite samples modified using NaCl solutions at different temperatures (T, 35 °C; solid concentration, 10 g/L; initial ammonium concentration, 0-400 mg/L; contact time, 24 h)

Exchange equilibrium isotherms: According to the experimental data in Figs. 3 and 5, the equilibrium relationships between the ammonium uptake of clinoptilolite and its equilibrium concentration in the solution are characterized by the exchange isotherms. To characterize the exchange equilibrium of ammonium for the natural and modified clinoptilolites, the Langmuir and Freundlich models were used. The equation of the Langmuir model is as follows:

$$\frac{C_t}{q_t} = \frac{1}{q_m} C_t + \frac{1}{k_L q_m} \quad (7)$$

where, q_t (mg/g) and C_t (mg/L) are the amount of ammonium exchanged by per unit mass of clinoptilolite 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 clinoptilolite and the Langmuir constant, respectively.

After fitting the experimental data with eqn. (7), the values of q_m and k_L were calculated from the slope and intercept of the plot, respectively. The results are given in Table-4. The values of q_m varied with the way in which the clinoptilolite was modified. The maximum amount of ammonium exchanged by the clinoptilolite modified with NaCl solution at 98 °C at equilibrium (q_m) was 19.92 mg/g.

TABLE-4
ISOTHERM CONSTANTS FOR AMMONIUM
EXCHANGE ON THE CLINOPTILOLITE

	Langmuir			Freundlich		
	q_m (mg/g)	k_L (L/mg)	R^2	k_f (mg/g)	1/n	R^2
Natural clinoptilolite	15.17	0.143	0.957	0.979	0.518	0.998
30 °C NaCl	17.61	0.077	0.967	1.959	0.414	0.998
50 °C NaCl	18.17	0.037	0.984	3.020	0.353	0.991
80 °C NaCl	18.91	0.025	0.989	3.597	0.339	0.991
98 °C NaCl	19.92	0.021	0.990	3.899	0.343	0.990
80 W ultrasonic	16.95	0.054	0.973	2.630	0.356	0.998
140 W ultrasonic	17.86	0.025	0.977	4.446	0.272	0.996
200 W ultrasonic	17.54	0.044	0.968	3.105	0.329	0.996
400 W ultrasonic	16.13	0.071	0.970	2.472	0.346	0.992

The Freundlich model is given by the following equation:

$$\log q_t = \log k_f + \frac{1}{n} \log C_t \quad (8)$$

where, k_f (mg/g) is the Freundlich constant indicating the exchange capacity of the adsorbent 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 eqn. (8), the Freundlich constants could be

calculated from the slope and intercept of the plot and the results are shown in Table-4. From Table-4, it was found that the Freundlich model yielded a much better fitting ($R^2 = 0.990-0.998$) of the data compared with the Langmuir model ($R^2 = 0.957-0.990$). 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 all of the clinoptilolite samples were smaller than 1, which indicated that the exchange conditions were favourable²⁷.

Conclusion

The removal of ammonium from aqueous solutions by Chinese Dalian clinoptilolite has been studied. The results have shown that a pseudo-second-order model gives a better correlation for all of the kinetic data as compared to Vermeulen's model or an intra-particle diffusion model. The correlation coefficient R^2 of the pseudo-second-order model reached 0.997. The optimal pH of solutions for ammonium exchange with the clinoptilolites was between 3 and 9, which can be mainly ascribed to the role of ion exchange. The use of aqueous NaCl solutions to soak the natural clinoptilolite samples increased their sodium contents and thus improved their ammonium-exchange capacities. The ammonium-exchange capacity of clinoptilolite could be improved by increasing the temperature of the aqueous NaCl solution in which it was soaked, but it could not be improved by increasing the power level of ultrasonication continuously. The highest uptake of ammonium was observed when the clinoptilolite was soaked with NaCl solution at 98 °C. It is easy to be applied. In addition, the Freundlich model provided a better fit of all of the ammonium-exchange equilibrium isotherms compared to the Langmuir model for both the natural and modified clinoptilolite samples.

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