

Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite

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Abstract

In this study, the Chinese natural clinoptilolite (sample 1) was fused with sodium hydroxide prior to hydrothermal reaction, and it was transformed to modified zeolite Na–Y (sample 2). The uptake of ammonium ion from aqueous solutions in the concentration range 50–250 mg NH₄⁺/l on to the two samples was compared and the equilibrium isotherms have been got. The influence of other cations present in water upon the ammonia uptake was also determined. The cations studied were potassium, calcium and magnesium. In all cases the anionic counterion present was chloride. The results showed that sample 2 exhibited much higher uptake capacity compared with sample 1. At the initial concentration of 250 mg NH₄⁺/l, the ammonium ion uptake value of sample 2 was 19.29 mg NH₄⁺ g⁻¹ adsorbent, while sample 1 was only 10.49 mg NH₄⁺ g⁻¹ adsorbent. For the natural clinoptilolite, the effect of the metal ions suggested an order of preference K⁺ > Ca²⁺ > Mg²⁺. These contrasted with the modified zeolite, where the order appeared to be Mg²⁺ > Ca²⁺ > K⁺.

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1. Introduction

Nowadays, the presence of nitrogen and phosphorus excess in the environment has caused eutrophication. Ammonia is usually found as ammonium ion (NH₄⁺) in aqueous solution. Common method for NH₄⁺ removal in wastewater is by air stripping and biological treatment [1,2]. However, as the discharge limits of different pollutants are more stringent, ion exchange is gaining on interest as available method for the treatment of waters polluted with ammonium ions.

Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment. Zeolites are hydrated aluminosilicates that possess a three-dimensional framework structure. This structure is formed by AlO₄ and SiO₄ tetrahedra that are connected by sharing an oxygen atom. When an AlO₄ tetrahedron is substituted for a SiO₄ tetrahedron, a neg-

ative charge appears which is neutralized by the exchangeable cations (Na⁺, K⁺, Ca²⁺, Mg²⁺). The discovery of natural zeolite deposits has lead to an increasing use of these minerals for the purpose of eliminating, or at least reducing, many long standing pollution problems [3–6].

Among natural zeolites, clinoptilolite occurs most frequently. Clinoptilolite is a silica-rich zeolite and has a lower ion exchange capacity. Further more, there are impurities like quartz in most of the clinoptilolite deposits. These factors reduce the uptake of ammonium ion onto natural clinoptilolite. Fusion with sodium hydroxide prior to hydrothermal reaction is the method to transform low-grade natural materials to high cation exchanger, which has been reported in several reports [7–9]. This method can dissolve the natural zeolites including impurities into silicate and aluminate with fusion, and get some high purity of zeolites with new frameworks after hydrothermal synthesis.

Besides ion exchange capacity, selectivity is also an important character for zeolites. The significant uptake of ions other than ammonium will reduce the effective uptake capacity for ammonium ion and thus the economics of the process. The cations chosen for this study were potassium, calcium and magnesium.

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They are always found in many natural waters and the water used in industrial recycle operations. Furthermore the ammonium ions coexist with them frequently in waste waters.

A range of studies has shown that clinoptilolite can be effective in removing ammonia from waste water [6,10,11]. Although the ion exchange capacity of clinoptilolite is lower than some other zeolites, it generally exhibits a high selectivity for NH_4^+ ion. However, there is some uncertainty on the selectivity differences between potassium, calcium and magnesium. Mc Veigh and Farkaš provided an order of preference $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ [10,12], whereas Weatherley and Miladinovic suggested $\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ [6]. It seems that natural clinoptilolites from various places have different characters.

The aim of the research here was first to transform low-grade Chinese natural zeolite to high cation exchanger, then to measure and compare the equilibrium uptake of ammonium ion onto the two materials. The effect of the individual presence of potassium, calcium and magnesium ion upon ammonium ion uptake onto each sample was also investigated.

2. Materials and methods

2.1. Reagents

All chemicals were of analytical grade. NH_4Cl , KCl , CaCl_2 , and MgCl_2 were all prepared into 1000 mg cations/l stock solution. Deionized water was used throughout the experiments.

2.2. Zeolites characterization

The natural clinoptilolite (light grayish white) was collected at Jinyun, Zhejiang, PR China. The chemical composition of the mineral is shown in Table 1 [13]. The natural zeolite was prepared as a sample for the present experiment after crushing, air-drying and passing through a 74 μm sieve.

Under investigation, we choose the optimal condition to synthesize the modified zeolite [9]. 7.5 g of the natural zeolite powder was placed in a Ni crucible and fused with 9 g of NaOH powder at 550 °C for 2 h. The melt was ground and 75 ml of water was added so as to prepare the NaOH solution of 3 mol/l. The mixture was homogenized, transferred into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 8 h. The prod-

ucts were filtrated and stirred with 50 ml 1 mol/l NaCl . In order to remove the alkali absorbed by the zeolite, 1 mol/l HCl was dropped into the mixture until the pH got to 6. The products were filtrated and dried.

2.3. Analytical methods

Identification of mineral species in the zeolite samples was carried out by X-ray diffraction (XRD) of the random-oriented powder samples using Siemens X-ray diffractometer D5005 (Cu $\text{K}\alpha$ radiation, $2\theta = 5\text{--}40^\circ$).

An IRIS Intrepid II XSP Inductively Coupled Plasma Atomic Emission Spectroscopy determined the content of Si and Al in samples 1 and 2.

The exact concentrations of ammonium ions in the solutions were determined by Nesslerization [14]. And the solid-phase concentrations determined by mass balance, according to Eq. (1):

$$Q_e = \frac{V}{M}(C_0 - C_e) \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of ammonium in the liquid phase (mg/l), respectively, Q_e the solid-phase concentration of ammonium (mg/g), V the volume of solution (l), and M is the mass of dry zeolite (g).

2.4. Equilibrium batch experiments

All sorption studies were carried out in beakers of 250 ml by subjecting a given dose of sorbent to a period of stirring with ammonium solution on a magnetic stirrer (800 turns/min). After adsorption, the sorbent was separated by centrifugal machine (2000 turns/min).

The scope of the experimental work was confined to determination of the equilibrium uptake behaviour of ammonium ion on to natural and modified zeolites in the presence of chloride co-ion. During all experimental work the pH was maintained at a value of 6–7. It was assumed that all ammonia existed in the ionic form and was available for ion exchange.

2.4.1. Equilibrium studies

One gram samples of zeolite were continuously stirred with 100 ml of ammonium chloride solution, having concentrations in the range 50–250 mg NH_4^+ /l. The ammonia levels were measured every 1 h over a period of 8 h. Preliminary experiments showed that up to 5 h contact were required for equilibrium to be reached.

2.4.2. Influence of individual presence of K^+ , Ca^{2+} and Mg^{2+} ions

In order to establish the extent to which the presence of potassium, calcium and magnesium ions influenced ammonium ion uptake, further equilibration experiments were conducted. These were confined to determination of the effect of each individual ion alone upon ammonium ion uptake. The starting solutions were dosed with the appropriate metal cation at a concentration of 100 mg/l and equilibration in the presence of ammonium ion

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

SiO_2	65.52
TiO_2	0.21
Al_2O_3	9.89
Fe_2O_3	1.04
MnO	0.06
MgO	0.61
CaO	3.17
Na_2O	2.31
K_2O	0.88
H_2O	7.25
LOI	10.02

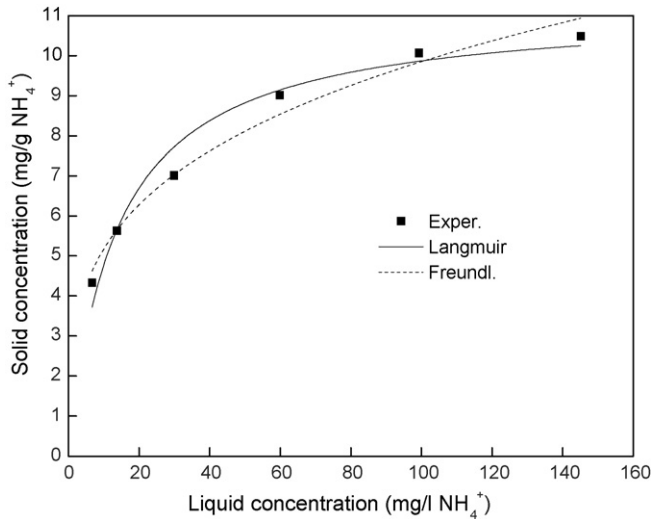


Fig. 1. Equilibrium isotherm data for ammonium uptake onto the natural clinoptilolite fitted to the Langmuir and the Freundlich uptake models: stirring time = 5 h.

50–250 mg/l. Equivalent concentrations for each metal were as follows: $100/39 = 2.6$ mequiv. K/l, $(100 \times 2)/40 = 5$ mequiv. Ca/l and $(100 \times 2)/24 = 8.3$ mequiv. Mg/l.

3. Results and discussion

3.1. The ion exchange capacity of the two zeolites

The equilibrium isotherms of the two materials are shown in Figs. 1 and 2. The modified zeolite had much higher ion exchange capacity than the natural zeolite. At the initial concentration of 250 mg NH_4^+ /l, the ammonium ion uptake value of sample 2 was 19.29 mg NH_4^+ /g, while sample 1 was only 10.49 mg NH_4^+ /g. It can be explained by their XRD pattern in Fig. 3 and the Si/Al molar ratios. The natural zeolite is composed of clinoptilolite and quartz (pore diameter: 4.6 Å; Si/Al molar

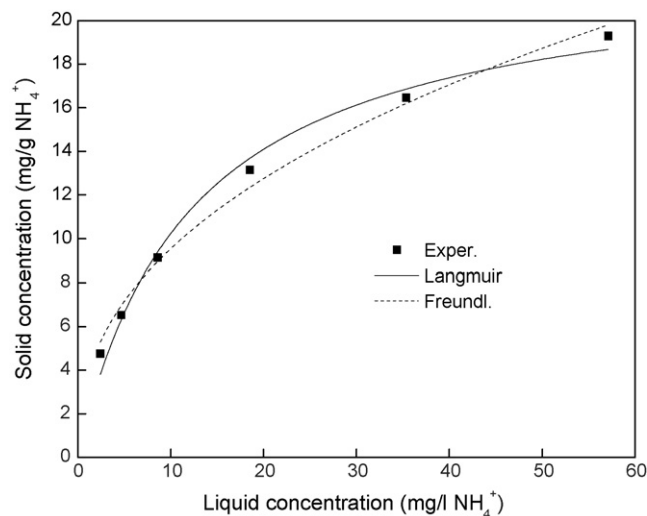


Fig. 2. Equilibrium isotherm data for ammonium uptake onto the modified zeolite fitted to the Langmuir and the Freundlich uptake models: stirring time = 5 h.

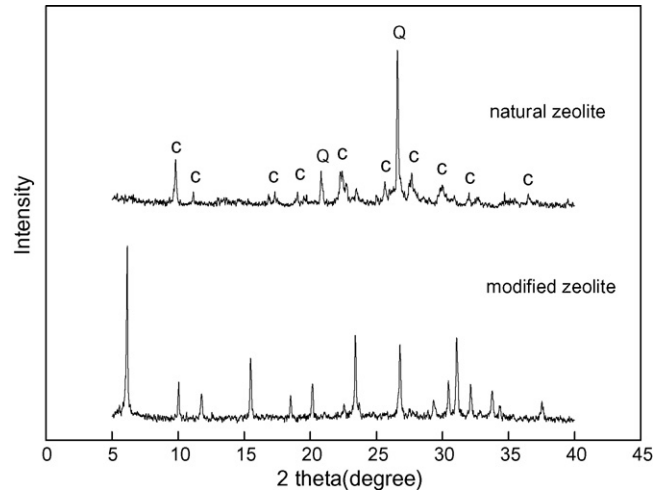


Fig. 3. The XRD patterns of the two materials—C: clinoptilolite and Q: quartz.

ratio: 4.8). The structure of quartz consists of corner-sharing SiO_4 tetrahedra, each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. It has no ion exchange capacity for absence of exchangeable cations. From the peak intensities we can find that the content of quartz is high, that reduces the uptake of ammonium ion onto it. Sample 2 is high purity of zeolite Na–Y (pore diameter: 7.4 Å; Si/Al molar ratio: 2.3). With bigger aperture and lower Si/Al molar ratio in framework, the ion exchange capacity was greatly increased.

3.2. The equilibrium isotherms of the two zeolites

Adsorption isotherm are essential for the description of how NH_4^+ concentration will interact with zeolites and are useful to optimize the use of zeolites as adsorbents. Therefore, empirical equations (Langmuir and Freundlich isotherm model) are important for adsorption data interpretation and predications. Both Freundlich and Langmuir models were used for the evaluation of experimental results.

The Langmuir model assumes only one solute molecule per site, and also assumes a fixed number of sites. The Langmuir isotherm relates Q_e (mg of ammonia absorbed per gram of zeolite) and C_e (the equilibrium ammonium concentration in solution) as shown in Eq. (2)

$$Q_e = \frac{KbC_e}{1 + KC_e} \quad (2)$$

Q_e was calculated from the volume of ammonia solution, the mass of the material exposed to the solution and the equilibrium ammonium concentration in the solution (C_e).

Rearranging the Langmuir equation gives Eq. (3), which is linear.

$$\frac{1}{Q_e} = \frac{1}{KbC_e} + \frac{1}{b} \quad (3)$$

The coefficients K and b can thus be determined by plotting $1/C_e$ versus $1/Q_e$.

Table 2
Values for the Langmuir and Freundlich coefficients for the two zeolites

	Natural zeolite	Modified zeolite
Langmuir parameter		
b (mg/g)	11.202	22.642
K (l/mg)	0.074	0.082
r^2	0.968	0.989
Freundlich parameter		
k	2.710	3.639
$1/n$	0.280	0.419
r^2	0.982	0.991

The Freundlich isotherm relates the uptake of solute onto the exchanger to the solution concentration, as shown in Eq. (4)

$$Q_e = kC_e^{1/n} \quad (4)$$

This isotherm can also be presented by the following equation:

$$\log Q_e = \log k + \frac{1}{n} \log C_e \quad (5)$$

When $\log Q_e$ is plotted against $\log C_e$ the coefficients k and n can be calculated. Knowing all coefficients and using experimental data for C_e , the Langmuir and Freundlich theoretical Q_e can be calculated according to Eqs. (2) and (4).

Figs. 1 and 2 show the equilibrium isotherm data for ammonium uptake onto the two zeolites, with each fitted to the Langmuir and Freundlich uptake models. Values for the coefficients calculated by experimental data and Eqs. (3) and (5) are given in Table 2.

For the two zeolites, the Freundlich model provides a slightly more consistent fit to the data compared with the Langmuir. In Langmuir equation, coefficient b represents the maximum amount that can be sorbed. Furthermore, k is Freundlich constant that is an index to the sorption capacity of sorbent. Both the values for b and k indicated that the modified zeolite has the higher sorption capacity than the natural zeolite.

3.3. The effect of the individual presence of other metals

The experimental uptake equilibrium data for natural clinoptilolite are shown in Fig. 4. The relationships between exchanger-phase concentration and solution-phase concentration are shown for the case of ammonium ion only, and for ammonium ion in the individual presence of potassium, calcium and magnesium ions.

The results show that in each case there is a significant reduction in the equilibrium uptake of ammonium ion in the presence of the other ion. The reduction has the order of $K^+ > Ca^{2+} > Mg^{2+}$, that is opposite to the order of equivalent concentrations $Mg^{2+} > Ca^{2+} > K^+$ (100 mg/l equals 2.6 meq K/l, 5 meq Ca/l and 8.3 meq Mg/l). It indicates that the natural clinoptilolite exhibits a high selectivity and the effect of the metal ions suggests an order of preference $K^+ > Ca^{2+} > Mg^{2+}$. It's consistent with the results of Mc Veigh and Farkaš [10,12].

The analogous ion uptake equilibrium data for the modified zeolite are shown in Fig. 5. From the results we can notice that in each case there is a significant reduction in the equilibrium uptake of ammonium ion in the presence of the other

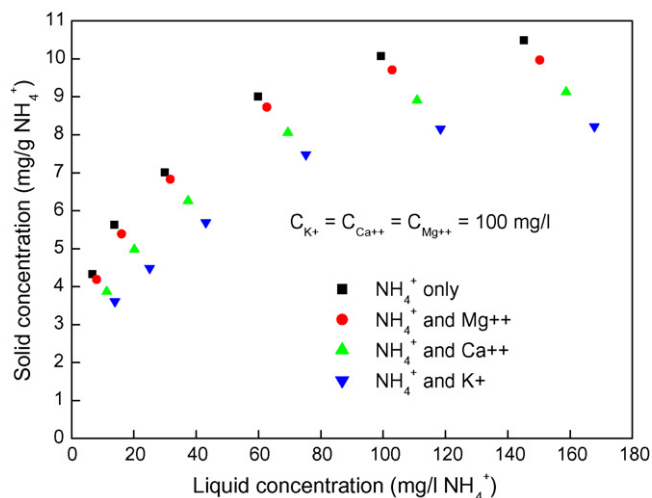


Fig. 4. Ammonium ion uptake onto clinoptilolite, in the presence of potassium, calcium and magnesium ions.

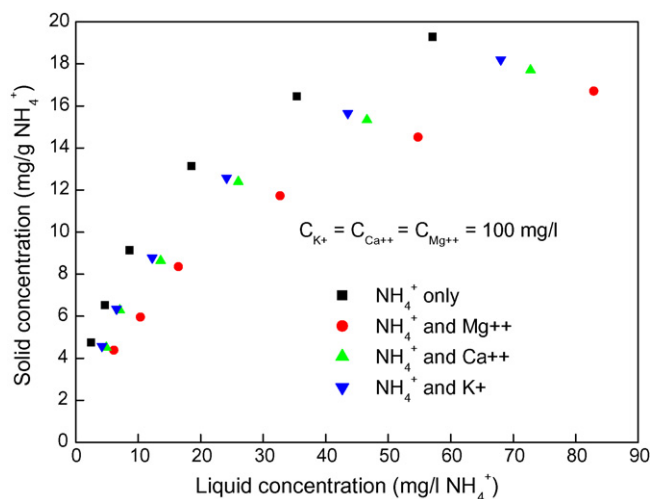


Fig. 5. Ammonium ion uptake onto the modified zeolite, in the presence of potassium, calcium and magnesium ions.

ion. The effect of the metal ions suggests an order of preference $Mg^{2+} > Ca^{2+} > K^+$. This could be due to the fact that the equivalent concentrations has the order of $Mg^{2+} > Ca^{2+} > K^+$. It seems that the modified zeolite exhibits a low selectivity for these cations than the natural clinoptilolite. The reason for this is that Na–Y has much bigger aperture than clinoptilolite and the ionic strength in the solution turns into the principal factor in ion exchange. Despite the low selectivity, sample 2 still has much higher ammonium ion uptake than sample 1 in the presence of other ions for its great ion exchange capacity.

4. Cost evaluations

One tonne of natural zeolites cost 50 dollars, and then treatment of 1 tonne natural zeolites will need 1.2 tonnes of NaOH (about 180 dollars). The total energy consumed needs 25 dollars. Furthermore, the yield of the modified zeolite is about 55% based on the initial natural zeolite input. So the cost of 1 tonne modified zeolites is about 460 dollars.

5. Conclusions

Fusion with sodium hydroxide prior to hydrothermal reaction, the Chinese low-grade natural zeolite was transformed to pure zeolite Na–Y. The results of this work underline the difference of uptake of ammonium ion onto these two materials.

With lower Si/Al molar ratio and higher purity, the modified zeolite had much higher ion exchange capacity than the natural zeolite. At the initial concentration of 250 mg NH₄⁺/l, the ammonium ion uptake value of modified zeolite was 19.29 mg/g NH₄⁺, while the natural zeolite was only 10.49 mg/g NH₄⁺.

Adsorption isotherms of the two materials were similar. The Freundlich model provides a slightly more consistent fit to the data compared with the Langmuir.

For the natural clinoptilolite, the presence of potassium ion had the most significant effect upon ammonium ion uptake, followed by calcium. Magnesium ion had the least effect.

The results showed that the modified zeolite had a low selectivity for these cations than the natural clinoptilolite. The effect of the metal ions upon ammonium uptake suggests an order of preference Mg²⁺ > Ca²⁺ > K⁺, that is the same order as the cation equivalent concentrations. The reason for this is that Na–Y has bigger aperture than clinoptilolite.

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