



Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent

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ABSTRACT

This paper presents a study of the removal of ammonium ion from aqueous solutions using natural Chinese (Chende) zeolite. A series of experiments was conducted to examine the effects of solution pH, particle size, contact time, adsorbent dosage, and the presence of other cation- and anion species on ammonium removal. The findings indicated that these parameters named had a significant effect on the removal of ammonium by the zeolite. The effect of other cations on the removal of ammonium followed the order of preference $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ at identical mass concentrations, and the effect of the presence of individual anions followed the order of preference carbonate > chloride > sulfate > phosphate at identical mass concentrations of ammonium ions. Kinetic analysis showed that the adsorption of ammonium on zeolite at different ranges of particle size well followed the pseudo-second-order model and followed the intra-particle diffusion model only during the initial 60 min of the adsorption process. Equilibrium isotherm data was fitted to the linear Langmuir- and Freundlich models with the latter model providing the better description of the process ($R^2 = 0.991\text{--}0.997$) compared to the former ($R^2 = 0.902\text{--}0.989$).

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1. Introduction

Nitrogen compounds are nutrients essential to all forms of life, but when present in substantial quantities in receiving waters such as lakes and rivers can cause their eutrophication, resulting in excessive growth of algae and other microorganisms, as well as in increased dissolved oxygen depletion and fish toxicity. As the eutrophication of waters becomes more frequent, the removal of nitrogen nutrients gains greater importance in wastewater treatment.

Commonly, nitrogen removal is achieved by a biological-, nitrification–denitrification process, where ammonium (NH_4^+) is transformed first to nitrite, then to nitrate, and finally to nitrogen gas [1]. However, since biological methods do not respond well to shock loads of ammonia, unacceptable peaks over the discharging levels may frequently appear in the effluent NH_4^+ concentrations [2]. Besides this, the treatment of ammonium nitrogen wastewater of low organic content by a biological process usually needs to be supplemented with a carbon source, which may add to the treat-

ment cost. In such a situation, ion-exchange offers an alternative method for the removal of NH_4^+ .

Ion-exchange has been in use in various types of wastewater treatment for the removal of NH_4^+ [3–10]. However, ion-exchange processes using organic resins as exchanger are very expensive. Hence, cheaper materials such as zeolite and sepiolite are needed [11]. The use of natural zeolite for the removal of NH_4^+ is considered to be a competitive and effective treatment method due to its low cost and relative simplicity of application and operation [2,12,13]. Natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina- and silica tetrahedra which result in an open and stable three-dimensional honeycomb structure [14] possessing high cation exchange capacity (CEC), cation selectivity, higher void volume, and great affinity for NH_4^+ [15]. In the use of natural zeolite, the factors which influence NH_4^+ removal performance are mainly pH, temperature, reaction time, initial concentration of NH_4^+ ions, adsorbent dosage, and other cations and anion species present in water, and so on. Although many previous studies have focused on these factors [11,14,16–19], each special zeolite material has its special characteristics and still requires to be researched individually.

The objective of this paper was to study the effects of pH, reaction times, adsorbent dosages, and particle size on NH_4^+ removal using a natural Chinese (Chende) zeolite, which is one of the important zeolites in China. Real wastewater is a complex solution. Other species of cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and anions

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(phosphate, chloride, sulfate and carbonate) when present in such complex solutions generally coexist with NH_4^+ in many types of wastewaters. Therefore, we investigated the influence of the individual presence of such species of cations and anions upon NH_4^+ uptake onto zeolite. In addition, adsorption kinetics and equilibrium isotherms of the uptake of NH_4^+ ion on zeolite were studied.

2. Materials and methods

2.1. Materials

The natural zeolite media used in the experiments were obtained from Chende, Hebei, China, and supplied by North Mining Processing Plant. The mineralogical composition of the zeolite was determined by using Philips Model PW1830 X-ray diffractometer; the results obtained were as follows: 46% heulandite, 30% illite and 24% is montmorillonite. The cation exchange capacity of the zeolite ($0.074 \text{ mm} \leq d \leq 0.2 \text{ mm}$) was found to be 0.82 meq/g. The analysis of the chemical composition of the zeolite furnished by the manufacturer is shown in Table 1. The natural zeolite samples for the present experiments were prepared by grinding the zeolite to a series of grain sizes in the following ranges: 0.074–0.125 mm, 0.125–0.2 mm, and 0.2–0.3 mm. The samples were washed with de-ionized water to remove the water-soluble residues and other undesirable material and dried in an oven at $100 \pm 5^\circ\text{C}$ for 24 h.

2.2. Experimental methods

Preliminary conditional experiments were first conducted to obtain the optimum values of pH, particle size, contact time, and adsorbent dosage for the NH_4^+ ion removal from an aqueous solution with NH_4^+ concentration of 80 mg/L, which was prepared by dissolving ammonium chloride of analytical grade in distilled water. Subsequently, experiments were performed to study the effect of each individual cation (K^+ , Ca^{2+} , Na^+ and Mg^{2+}) present in the NH_4^+ ion solution on NH_4^+ removal by zeolite. Solutions with an NH_4^+ ion concentration of 80 mg/L and individual cation concentrations in the range of 0–250 mg/L were used. Stock solutions with a cation concentration of 10 g/L were added to the NH_4^+ ion aqueous solutions for preparing working solutions. KCl, CaCl_2 , NaCl and MgCl_2 of analytical grade were used to prepare these stock solutions. Distilled water was used in all experiments. The experiments with individual anions (phosphate, sulfate, chloride, and carbonate) present alone in the NH_4^+ ion solution were carried out using solutions prepared individually with $(\text{NH}_4)_2\text{HPO}_4$, NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{CO}_3$ of analytical grade, with NH_4^+ ion concentrations varying in the range of 50–300 mg/L. In this study, the sorption equilibrium isotherms and adsorption kinetics were also determined. The experimental procedure followed was as below: a 500 ml breaker was placed on a magnetic stirrer and into which 250 ml of NH_4^+ ion solution was first poured; a given dose of

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

Constituent	Value (%)
SiO_2	71.53
Al_2O_3	13.65
Fe_2O_3	2.82
TiO_2	0.28
CaO	1.89
MnO	0.05
MgO	1.61
Na_2O	1.86
K_2O	4.14
Loss of ignition	5.60

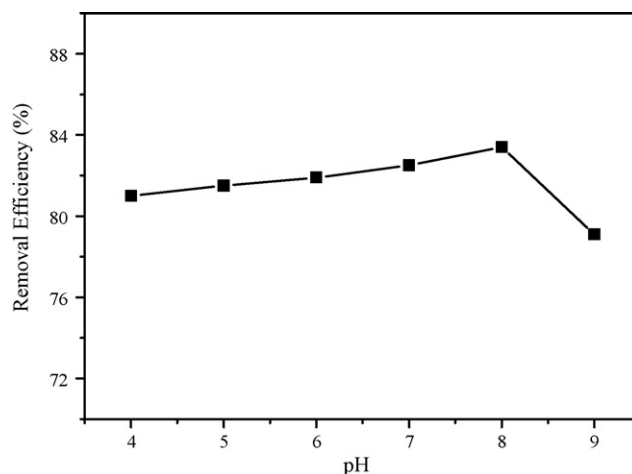


Fig. 1. Effect of pH on the removal of NH_4^+ ion (adsorbent dosage: 24 g/L; contact time: 60 min; particle size: 0.125–0.2 mm; initial ammonium concentration: 80 mg/L).

natural zeolite adsorbent was then added into this aqueous solution. The experiments were performed at room temperature (27°C) with the solutions stirred at a rate of 500 rpm; pH was adjusted to the value desired by the addition of 0.1 M NaOH or 0.1 M HCl stock solutions. After adsorption, samples were filtered through a $0.45 \mu\text{m}$ filter membrane. The filtrates obtained were analyzed by the conventional Nesslerization method to determine the NH_4^+ ion concentration remaining in the aqueous solution [20]. Metal cations (K^+ , Ca^{2+} , Na^+ and Mg^{2+}) were measured with an atomic adsorption photometer (Shimadzu AA-6800, Japan). The removal efficiency (%) of zeolite and the amount of adsorbed NH_4^+ ions (q_e) by it were calculated, respectively, using the following equations:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e (mg/g) is the amount of adsorbed NH_4^+ ion on zeolite, C_0 and C_e are the starting and final equilibrium concentrations of NH_4^+ ion in solution (mg/L), respectively. V is the volume of the working solution (L) and m is the mass of added zeolite (g).

3. Results and discussion

3.1. The effect of pH

NH_4^+ ion removal by natural Chende zeolite was observed at pH values ranging between 4 and 9. The results are depicted in Fig. 1. The figure shows that as solution pH increases in the range of 4–8, the removal efficiency of NH_4^+ ion increases gradually and reaches a maximum value (83.4%) when the pH value is 8. When the pH increases to 9, the removal efficiency drops dramatically (79.1%). This finding tallies with the observations reported by previous authors [11]. This behavior can be explained by the fact that at pH values above 8 partial dissolution of the natural zeolite occurs, and it is also likely that NH_4^+ is converted into NH_3 specimen [11,15,21]. Although, at pH values below 8, the NH_4^+ ion concentration in solution rises when pH decreases there nevertheless results a decline in removal efficiency, as the H^+ ion concentration also rises with the decrease in pH and intensifies competition for exchange sites.

Table 2
Rate constants and correlations coefficients for the studied kinetic models.

Particle size of adsorbent (mm)	Pseudo-second-order model			Intra-particle diffusion model	
	k_2 (g/(min mg))	q_e (mg/g)	R^2	k_i (mg/(min ^{1/2} g))	R^2
0.074–0.125	0.375	2.89	1.00	0.028	0.945
0.125–0.2	0.155	2.86	1.00	0.068	0.970
0.2–0.3	0.126	2.83	1.00	0.100	0.919

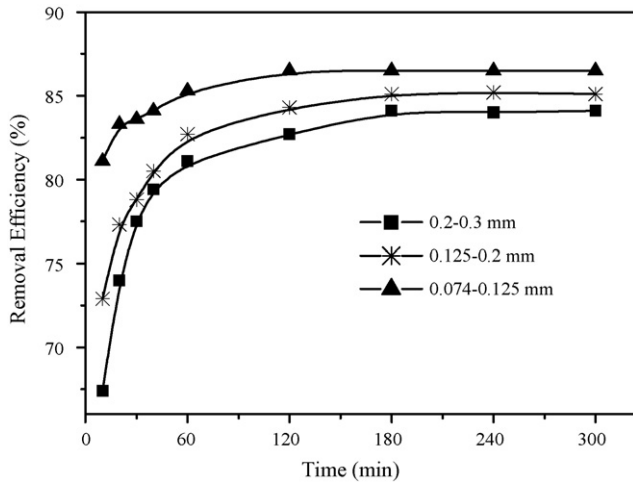


Fig. 2. Effects of particle size on the removal of NH_4^+ ion at different contact times (adsorbent dose: 24 g/L; pH: 8; initial ammonium concentration: 80 mg/L).

3.2. The effects of particle size and contact time and ammonium adsorption kinetics

The results of experiments to determine the effects of particle size, in contact times ranging between 10 min and 300 min are shown in Fig. 2; they reveal that NH_4^+ ion removal efficiency rises with decrease in particle size and increase in the contact time. It was observed that removal efficiency of NH_4^+ ion rose from 67.4% to 81.1% within 10 min with reduction in the zeolite particle size range from 0.2 to 0.3 mm to 0.074–0.125 mm. This is because the smaller the particle size the greater the specific surface area, which promotes external surface adsorption, and implies that the cations in zeolite of smaller particle size are exchanged much more easily with those in the aqueous solution [19]. Moreover, the removal efficiencies of NH_4^+ ion by zeolite of different particle sizes were initially a fast process with over 80% of the removal being achieved within the first 60 min. Thereafter, with increase of contact time

the rate of removal slowed down considerably and after passage of 120 min was almost negligible. This behavior may be ascribed to the quick utilization of the most readily available adsorbing sites of the zeolite leading to fast diffusion and attainment of rapid equilibrium [2]. After approximately 180 min of adsorption, sorption equilibrium begins to establish itself for all the three zeolites of different particle size ranges. On the basis of these results and analysis, a 180-min contact period and the particle size range of 0.074–0.125 mm were selected for subsequent studies.

To study the adsorption mechanism of NH_4^+ ion uptake onto the zeolite, the pseudo-second-order kinetic model and the intra-particle model were used; the kinetic equation of the pseudo-second-order model is as follows [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where the k_2 is the rate constant of pseudo-second-order model (g/(min mg)), q_t and q_e are the amounts of NH_4^+ ion adsorbed onto zeolite at time t and at equilibrium (mg/g), respectively. The values of k_2 and q_e can be calculated from the slope and the intercept of the straight-line plots of t/q_t versus t and are noted in Table 2. The plots of the pseudo-second-order kinetic for different ranges of particle size are shown in Fig. 3a. As seen from Table 2, the high correlation coefficients ($R^2 = 1$) obtained confirmed that the adsorption of NH_4^+ ion on zeolite could well follow the pseudo-second-order kinetic model.

The intra-particle diffusion is represented by:

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

where k_i is the intra-particle diffusion rate constant (mg/(min^{1/2} g)), q_t is the amount of NH_4^+ adsorbed at the time of t (mg/g), and C is the intercept. The intra-particle diffusion model as fitted with the experimental data is presented in the plot of q_t versus $t^{1/2}$ depicted in Fig. 3b, and the values of k_i and correlation coefficients are given in Table 2. NH_4^+ adsorption by zeolite involves two stages: surface sorption and intra-particle diffusion [2]. As can be seen from Fig. 3b, the intra-particle diffusion model can be only applied to describe NH_4^+ adsorption on the zeolite

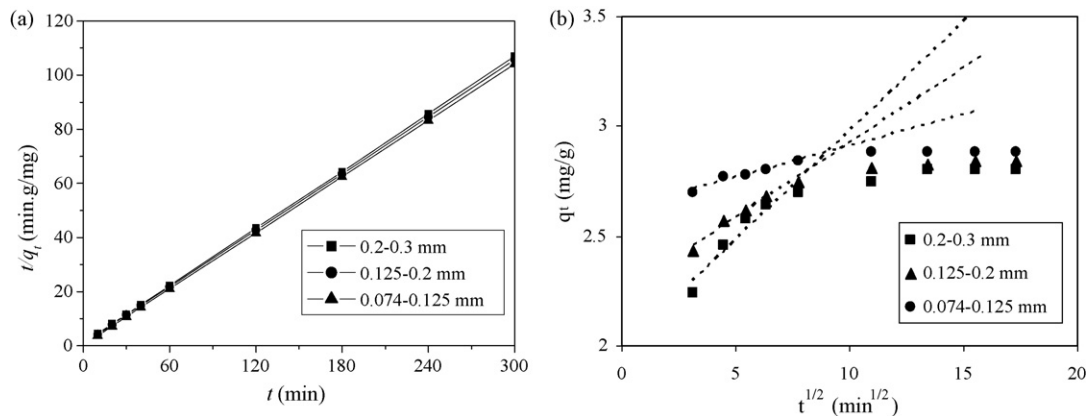


Fig. 3. (a) Pseudo-second-order kinetic model for NH_4^+ adsorption onto zeolite at different particle sizes; (b) intra-particle diffusion model for NH_4^+ adsorption onto zeolite at different particle sizes.

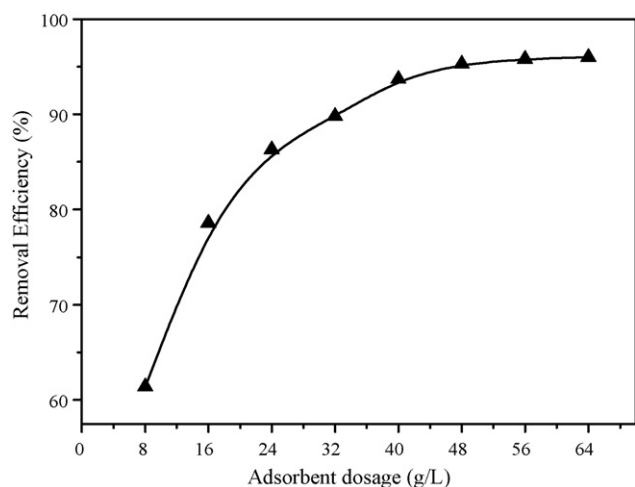


Fig. 4. Effect of adsorbent dosage on the removal of NH_4^+ ion (contact time: 180 min; pH: 8; initial ammonium concentration: 80 mg/L; particle size: 0.074–0.125 mm).

during the initial 60 min. During this 60-min period, adsorption of NH_4^+ by the zeolite proceeds mainly by boundary layer diffusion and thereafter mainly by intra-particle diffusion. This tallies with the results reported by previous authors [7,22].

3.3. The effects of adsorbent dosage

The results of experiments to determine the effects of adsorbent dosage on NH_4^+ removal are shown in Fig. 4 and reveal that the removal efficiency of NH_4^+ ion by the zeolite increased with an increase in adsorbent dosage. It rose from 61.4% to 96% with the increase of adsorbent dosages ranging from 8 g/L to 64 g/L. While a rapid increase was observed at adsorbent dosages ranging between 8 g/L and 48 g/L, a plateau was seen at those ranging between 48 g/L and 64 g/L. Increasing adsorbent dosage above 48 g/L had negligible effect on the increase in removal efficiency of NH_4^+ ions. This may be attributed to the formation of aggregates at higher solid/liquid ratios or to precipitation of particles [11].

3.4. The effects of the individual presence of other metal cations

The experimental results obtained for NH_4^+ removal by natural zeolite in the individual presence of potassium, calcium, sodium and magnesium ions are shown in Fig. 5, which reveal that there is a significant reduction in the removal efficiency of NH_4^+ ion in the presence of other metal ions. As shown in Fig. 5, when the concentrations of Mg^{2+} , Ca^{2+} , K^+ and Na^+ increased from 0 mg/L to 250 mg/L, the removal efficiency of NH_4^+ ions decreased from 95.3% to 91.2%, 86.8%, 84.1%, and 83.3%, respectively. At identical concentration of metal cations, the removal efficiency of NH_4^+ ion was highest for Mg^{2+} present in the solution, followed by Ca^{2+} , K^+ and Na^+ .

When no other cations were present in the solution, the equivalent concentrations of Na^+ , K^+ , Ca^{2+} and Mg^{2+} transferred from the zeolite to the solution are measured, as given in Table 3, after the

Table 3
Equivalent concentrations of cations in the solution after exchange reaction.

Cation	Equivalent concentration (meq/L)
K^+	0.05
Ca^{2+}	0.6
Na^+	3.6
Mg^{2+}	0.3

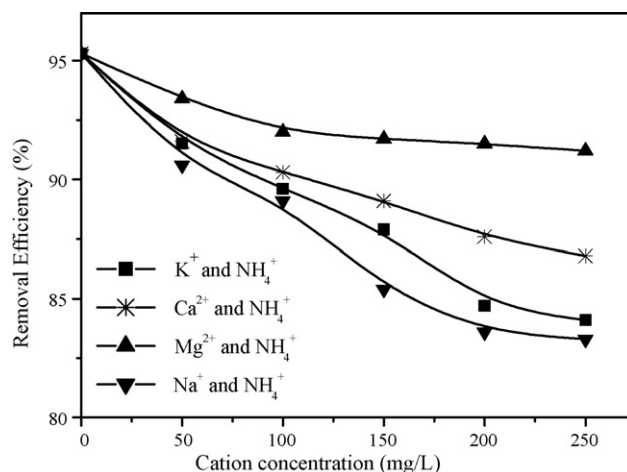


Fig. 5. Effects of cations on the removal of NH_4^+ ions (adsorbent dose: 48 g/L; contact time: 180 min; particle size: 0.074–0.125 mm; pH: 8; starting ammonium concentration: 80 mg/L).

completion of the reaction. This suggested that the removal of the NH_4^+ ions from the aqueous solution using the natural zeolite is mainly carried out by the following ion-exchange reaction:



With an increase in the concentration of Na^+ ions in the solution, the reaction takes place from right to the left, thereby resulting in a significant decrease in the ammonium uptake [22]. As a result, the competitive effect of Na^+ was greatest for ammonium adsorption. When K^+ , Ca^{2+} and Mg^{2+} were individually present in the solution, the uptake of ammonium decreased because the cations present in the solution compete with NH_4^+ ions for adsorption on the zeolite, and this competition increases with the starting concentration of metal cations. Additionally, as the order of ionic radii is $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, the available pore size of formed K^+ -zeolite was smaller than those of Ca^{2+} -zeolite and Mg^{2+} -zeolite formed. This led to a decrease in the rate of diffusion of NH_4^+ in the pores [23]. Hence, it was concluded that the order of the effect of metal cations on NH_4^+ ion removal is $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ at the same cation concentration. Similar results have also been previously reported by other authors [16,22,24].

3.5. The effects of anions and adsorption equilibrium isotherms

Fig. 6 shows the influence of anion species on NH_4^+ ion removal by natural zeolite. The results of experiments are presented as a function of the different starting concentrations of NH_4^+ ion. From Fig. 6, it seen that as the initial NH_4^+ concentration increased the removal efficiency of NH_4^+ ion decreased. This may be attributed to the adsorbent tending to become saturated and a consequent increase in the driving force required for further adsorption of NH_4^+ ion onto the zeolite. At identical NH_4^+ concentrations, the effect of carbonate present in solution on NH_4^+ removal was greatest, and was followed by those of chloride, sulfate, and phosphate in that order. When the initial NH_4^+ concentration was raised from 50 mg/L to 300 mg/L with carbonate present alone in the solution, the NH_4^+ ion removal efficiency fell from 92% to 67.8%; however, when phosphate, sulfate, and chloride were present, efficiency declined from around 95% to 89%, 83% and 81.2%, respectively. This suggested that the order of anion effect on NH_4^+ removal is carbonate > chloride > sulfate > phosphate. Marañón et al. [14] have reported that the effect of sulfate was higher than that of chloride. They reckoned that the size of anions may affect the adsorption of ammonium onto the surface of zeolite. However, this contradicts

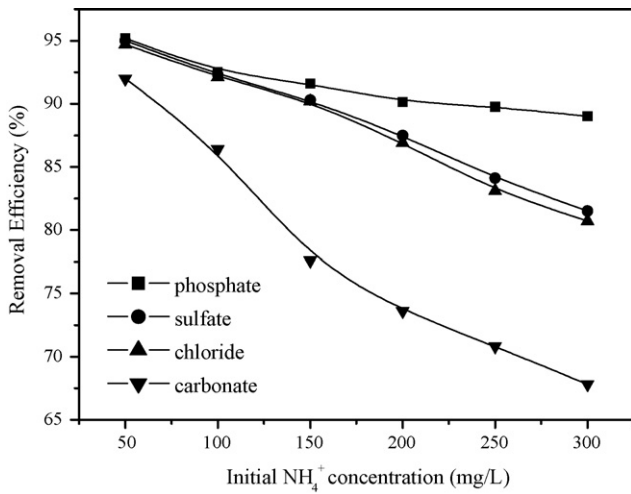


Fig. 6. Effects of anions on the removal of NH_4^+ ions (adsorbent dose: 48 g/L; contact time: 180 min; particle size range: 0.074–0.125 mm; pH: 8).

the results obtained from this study. Hence, the mechanism of the phenomenon needs to be further studied.

The ion-exchange isotherms characterize the equilibrium relationships between the amounts of exchanged ion by zeolite and its equilibrium concentration in the solution [25]. To characterize the exchange equilibrium of NH_4^+ ions by the zeolite in the individual presence of phosphate, sulfate, chloride and carbonate, the Langmuir and Freundlich models were used. The equation of the Langmuir isotherm is as follows:

$$\frac{C_e}{q_e} = \frac{1}{Mk_L} + \frac{C_e}{M} \quad (6)$$

where q_e (mg/g) and C_e (mg/L) are the amount of NH_4^+ adsorbed by per unit mass of zeolite at equilibrium and the NH_4^+ concentration in the solution at equilibrium, respectively; M (mg/g) and k_L (L/mg) are the maximum adsorption capacity of zeolite and the Langmuir constant, respectively. The linear plot of Langmuir isotherm is shown in Fig. 7. It is noted that the values of M and k_L were calculated from the slope and the intercept of the plot, respectively, and are given in Table 4. The value of M varied with the anion species present in the solution. The maximum amount of NH_4^+ adsorbed by the zeolite at equilibrium (M) was 9.41 mg/g in the individual presence of phosphate and 5.05 mg/g in the individual presence of carbonate.

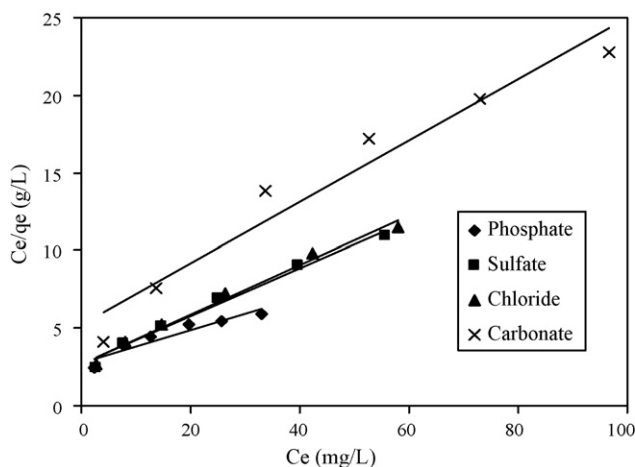


Fig. 7. Linear plot of Langmuir isotherm of NH_4^+ ion adsorption on natural zeolite.

Table 4
Isotherms constants for the ammonium exchange by the zeolite.

Anions	Langmuir parameter			Freundlich parameter		
	M (mg/g)	k_L (L/mg)	R^2	k_F (mg/g)	$1/n$	R^2
Phosphate	9.41	0.038	0.902	0.54	0.657	0.997
Sulfate	6.47	0.057	0.985	0.64	0.529	0.995
Chloride	6.32	0.058	0.989	0.63	0.521	0.991
Carbonate	5.05	0.029	0.953	0.51	0.457	0.995

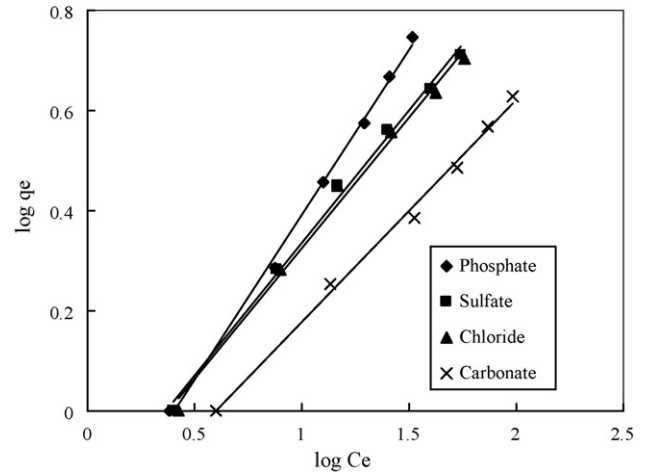


Fig. 8. Linear plot of Freundlich isotherm of NH_4^+ ion adsorption on natural zeolite.

The linear form of the Freundlich model is given by the following equation:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

where k_F (mg/g) is a Freundlich constant indicating the adsorption capacity of adsorbent, and $1/n$ is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the material [14]. Freundlich constants can be calculated from the slope and intercept of Fig. 8, and are given in Table 4. As seen in Table 4, it was found that the Freundlich model yields a much better ($R^2 = 0.991$ – 0.997) fit to the data compared with that of the Langmuir model ($R^2 = 0.902$ – 0.989). In addition, the $1/n$ constant for the Freundlich isotherm is a measure of exchange intensity or surface heterogeneity and ranges between 0 and 1. In this study, the values of $1/n$ for all anion species were less than 1 which suggested that the adsorption conditions were favorable [26].

4. Conclusions

The findings of this work indicated that basic conditions such as solution pH, particle size, contact time, and adsorbent dosage influence the removal of NH_4^+ ion from aqueous solutions by Chinese Chende zeolite. Moreover, the presence of other species of cations and anions in the solution can influence significantly the removal of NH_4^+ ion by the zeolite. The presence of Na^+ had the most effect on NH_4^+ ion removal, followed by K^+ , Ca^{2+} and Mg^{2+} ; hence, the order of preference that emerged was $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ at identical mass concentration of metal ions. In addition, the NH_4^+ removal efficiency of the Chende zeolite decreases with an increase in the concentration of NH_4^+ in solution; the effect of anion species present alone in solution on NH_4^+ removal had a decreasing order of preference, namely carbonate > chloride > sulfate > phosphate at identical NH_4^+ ion concentrations.

The pseudo-second-order kinetic model agreed very well with the dynamical data for the adsorption of NH_4^+ ion on zeolite;

however, the intra-particle diffusion model applied only during the initial 60 min of the adsorption process. The Langmuir- and Freundlich models were used to describe the isotherm data. The obtained results showed that Freundlich model had a much better ($R^2 = 0.991\text{--}0.997$) fit to the data compared to the Langmuir model ($R^2 = 0.902\text{--}0.989$). The value of $1/n$ obtained from the Freundlich isotherm indicated that the removal of NH_4^+ ions using zeolite is favorable.

Based on these findings, we can conclude that the Chende zeolite is suitable for the removal of NH_4^+ ions from aqueous solutions, especially solutions in which phosphate is present, and the process can be utilized for wastewater treatment.

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