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Ion-exchange process for ammonium removal and release using natural Iranian zeolite

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ABSTRACT

In this study, the ability to remove ammonium (NH_4^+) from aqueous solutions with different Na^+ concentrations (0.03, 0.1, and 0.3 M) by natural Iranian zeolite in millimeter and nanometer particle sizes was determined and the equilibrium isotherms were characterized. The effect of ionic strength on NH_4^+ release from Iranian zeolite was also evaluated and several kinetic models were tested. It was demonstrated that the initial NH_4^+ and Na^+ concentrations had significant effect on the amount of NH_4^+ exchanged. A decrease in Na^+ concentration resulted in greater amounts of NH_4^+ being exchanged and therefore resulted in greater removal efficiency. In addition, three parameter isotherm models (Redlich–Peterson and Langmuir–Freundlich) proved a better fit in terms of the coefficient of determination (R^2) and standard error of estimate (SEE) than two-parameter isotherm models (Langmuir and Freundlich), with the Langmuir model providing a better description of ion-exchange processes than the Freundlich model. NH_4^+ release was rapid for the first 60 min, but slowed thereafter, and also displayed a concomitant increase with the ionic strength of the solution. The NH_4^+ release data were successfully described by Elovich, power function, and pseudo second-order models, while the best fit was generally found between the experimental data and the Elovich model with R^2 and SEE ranging from 0.866 to 0.958 and 0.043 to 0.194, respectively. Based on the results, it can be suggested that the natural Iranian zeolite is a suitable ion-exchanger for NH_4^+ ion removal and consequently has potential as a controlled-release NH_4^+ fertilizer.

1. Introduction

The loss of nitrogen (N) from applied N fertilizer due to leaching, volatilization, and denitrification leads to not only a decrease in N fertilizer efficiency, but can also result in air and groundwater contamination (Cassman et al., 2002; Owens et al., 1992). Reduction in such loss has been one of the major issues in both agricultural and environmental studies. Among the approaches, the application of zeolites as a soil amendment to improve the physical and chemical properties of soil and to reduce the loss of nutrients and water has attracted intensive attention (Boettinger and Ming, 2002; Park and Komarneni, 1998). Natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina- and silica tetrahedral which result in an open and stable three-dimensional honeycomb structure (Maranon et al., 2006) possessing high cation exchange capacity (CEC), cation selectivity, higher void volume, and a great affinity for NH_4^+ (Dixon and Weed, 1989). Zeolites have also received great interest as they are able to minimize ammonia (NH_3) volatilization in soils with low CEC (He et al., 2002) and reduce NH_3 emissions from farm manure (Chlopecka and Adriano, 1997). In addition, they can serve as a gradual available source of nutrients (Park and Komarneni, 1998) and are often used as an inexpensive cation exchanger to minimize problems associated with nitrogen leaching during fertilizer application (Allen et al., 1996; Dwairi, 1998).

Ion exchange process is used in various fields in recent years, including wastewater treatment. However, ion exchange processes, which used organic resins, are very expensive. The aforementioned unique properties of zeolites, as well as its ready availability in many countries (Boettinger and Ming, 2002; Kazemian, 2002; Rehakova et al., 2004; Sarioglu, 2005), have resulted in its widespread use in ion exchange applications for the removal of several toxic substrates, such as heavy metal ions (Inglezakis et al., 2002) and dye contaminants (Kurama et al., 2002), from industrial and municipal wastewater. The use of zeolite for the removal of NH_4^+ ions from aqueous solutions and wastewater is particularly promising when compared with other processes involving biological or chemical treatment (Dimova et al., 1999; Wang et al., 2006).

Although a large number of studies on the removal of ammonium ions from aqueous solutions using zeolite have been performed, every special zeolite material requires individual research. Therefore

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understanding the ion-exchange and release processes in different sources of zeolite is important with respect to NH_4^+ ion removal from wastewater and farm manure, especially the urine of animals, reducing N losses via NH_3^+ volatilization and NO_3^- leaching in soils with increasing soil retention capacity for NH_4^+ and utilization of zeolite as a controlled release NH_4^+ fertilizer. Although zeolite tuffs are widely distributed in huge deposits in different regions of Iran (Kazemian, 2002), rare official reports are published on their use. In this regard, the following objectives were in this study: (1) determination of the effect of cation (Na^+) concentration on NH_4^+ removal by natural Iranian zeolite and identification of an empirical model that best describes this ion-exchange process; (2) determination of the effect of particle size on NH_4^+ removal; and (3) examination of ammonium release as a function of ionic strength and identification of an empirical model that best describes the release kinetics.

2. Experimental methods

2.1. Zeolite sample

The natural zeolite used in this study originated from Semnan province, Iran. Mineral identification using X-ray diffraction showed that the zeolite consisted mainly of clinoptilolite (Fig. 1). Total elemental analysis was performed by a Spectro X-Lab 2000 X-Ray fluorescence spectrometer. The zeolite had the following chemical composition (in %): $SiO_2 = 65.90$, $Al_2O_3 = 11.20$, $Na_2O = 2.10$, $K_2O = 2.31$, $CaO = 3.20$, $Fe_2O_3 = 1.25$, $MgO = 0.52$, Loss of ignition (LOI) = 11.89, and $SiO_2/Al_2O_3 = 5.9$. The particle size of the zeolite was between 0.2 and 0.8 mm. Most (99.85%) of the zeolite particles were smaller than 0.8 mm in diameter and the diameter of the 50% of zeolite particle (D_{50}) was about 0.6 mm. To obtain nano-sized mineral particles, the mineral was ground in a jet mill. Particle size was then determined using a particle size analyzer (Malvern Zetasizer 3000, UK). The reported size was about 300 nm (Fig. 2). The CECs of the millimeter- and nanometer-sized particles of Cp (Clinoptilolite) were 140 and 165 cmol kg^{-1}, respectively, as determined using a 1 M NH_4OAc saturation method (Chapman, 1965).

2.2. Ammonium removal procedure

In this study, the influence of Na^+ concentrations of 0.03, 0.1 and 0.3 M on NH_4^+ removal by Iranian zeolite of millimeter and nanometer particle sizes was investigated. The removal procedure for Na^+ concentration, using 0.03 M as an example, was as follows. To prepare working solutions, an ammonium chloride stock solution was prepared by dissolving the appropriate amount of NH_4Cl in a 0.03 M NaCl solution. Next, the appropriate amount of NH_4Cl stock solution was added to a 0.03 M NaCl solution to obtain NH_4^+ ion concentrations of between 90 and 3610 mg L^{-1}. For each 50-ml centrifuge tube, 1 g zeolite and 30 ml of working solution was mixed at 25 ± 1 °C for 2 h at 200 rpm. The mixtures were then centrifuged and the NH_4^+ was analyzed by a steam distillation procedure (Keeney and Nelson, 1982). All samples were prepared in triplicate. The NH_4^+ exchanged on zeolite was calculated using the equation (Lei et al., 2008):

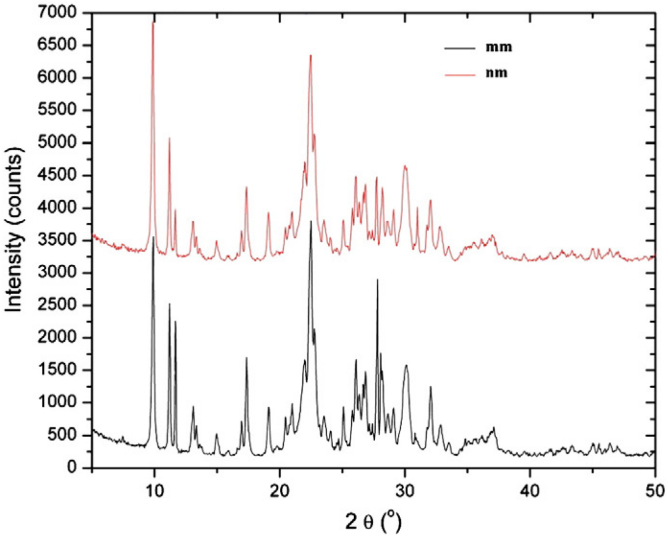


Fig. 1. XRD patterns of millimeter- (mm) and nanometer- (nm) sized zeolite particles.

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{1}$$

Where q_e is the NH_4^+ exchanged on zeolite (mg g^{-1}), M is the clinoptilolite mass (g), C_0 and C_e are the initial and equilibrium concentrations of NH_4^+ in solution (mg L^{-1}), respectively, and V is the volume of the solution (L). The removal efficiency was evaluated according to:

$$E = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

Where E is the ammonium removal efficiency expressed in %. To characterize the exchange equilibrium of NH_4^+ ions by zeolite, the Freundlich, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models were used as follows (Lei et al., 2008):

$$\text{Freundlich equation: } q = KC_e^{\frac{1}{n}} \tag{3}$$

$$\text{Langmuir equation: } q = \frac{bq_m C_e}{(1 + bC_e)} \tag{4}$$

$$\text{Redlich} - \text{Peterson equation: } q = \frac{aC_e}{(1 + bC_e^n)} \tag{5}$$

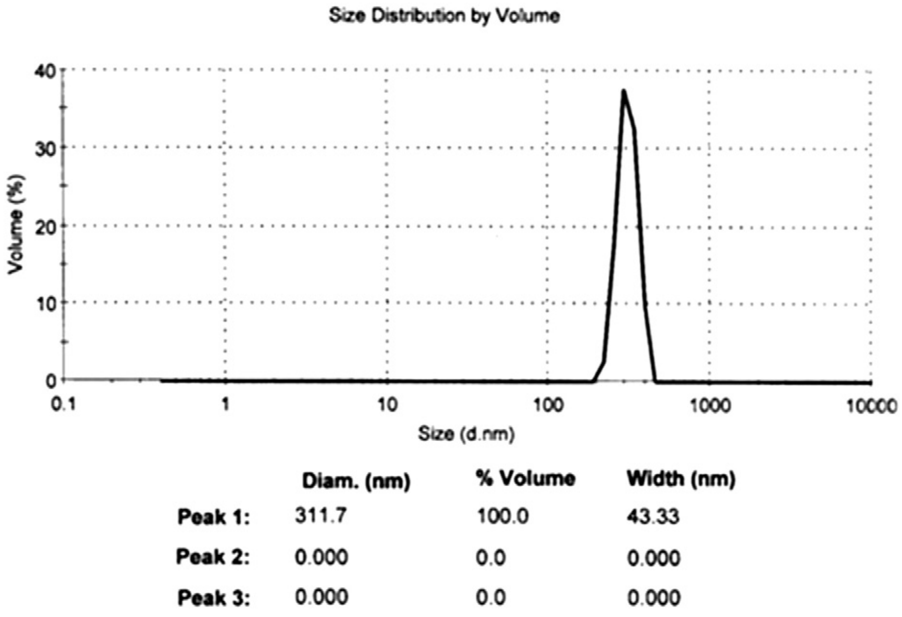
$$\text{Langmuir} - \text{Freundlich equation: } q = \frac{bq_m C_e^{\frac{1}{n}}}{(1 + bC_e^{\frac{1}{n}})} \tag{6}$$

Where q is the ammonium exchanged at equilibrium (mg NH_4^+/g) and C_e is the ammonium equilibrium concentration in solution (mg NH_4^+/L). The other parameters represent different isotherm constants that can be determined by regression of the experimental isotherm data. It has been reported that nonlinear regression analysis method is a better way of obtaining the parameters involved in three parameter isotherms (Kumar and Sivanesan, 2006). Therefore, the ion-exchange isotherms were examined by a non-linear curve fitting analysis method, using Data-fit software (Oakdale Engineering, trial version) (http://www.oakdaleengr.com/datafit.htm).

Previous studies have shown that commonly used correlation measures such as the correlation coefficient (R) and coefficient of determination (R^2) are often inappropriate or misleading when used to compare model estimated and measured data. Difference measures such as the standard error of estimate (SEE), however, contain appropriate and insightful information (Willmott, 1982). In this study, the goodness of fit between experimental and model-estimated data was evaluated using R^2 and the SEE as follows:

$$SEE = 1 - \left(\frac{\sum_{i=1}^{n} (q_e - q_p)^2}{n - 2} \right)^{1/2} \tag{7}$$

Where q_e and q_p are the measured and model estimated amounts of NH_4^+ exchanged, respectively, and n is the number of measurements. A lower SEE value and higher R^2 value are considered to represent goodness of conformity between measured and estimated NH_4^+ exchanged data.



	Diam. (nm)	% Volume	Width (nm)
Peak 1:	311.7	100.0	43.33
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

Fig. 2. The particle size distribution of nano-sized mineral.

2.3. Ammonium release procedure

The NH_4^+-loaded zeolite with millimeter particle size was used for release studies, which were conducted as a function of release time and different ionic strengths (deionized water (DW), 0.03, 0.1, and 0.3 M NaCl) in three replications. For each 50-ml centrifuge tube, 1 g of NH_4^+-loaded zeolite and 30 ml of deionized water or releasing solution with ionic strengths of 0.03, 0.1, and 0.3 were mixed for varying amounts of time (10, 30, 60, 90, 150, 200, and 300 min) at 25 ± 1 °C and 200 rpm, followed by centrifugation. All samples were prepared in triplicate. The supernatant was analyzed for released NH_4^+ at each time of agitation using a steam distillation procedure (Keeney and Nelson, 1982). The amount of released NH_4^+, described by Eqs. (8)–(11), as described in the later part (Shirvani et al., 2007):

$$\text{Pseudo first} - \text{order equation: } q_t = q_e(1 - e^{-k_1 t}) \tag{8}$$

$$\text{Pseudo second} - \text{order equation: } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

$$\text{Power equation: } q_t = at^b \tag{10}$$

$$\text{Elovich equation: } q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \tag{11}$$

Where q_t is the amount of ammonium released at time t (mg NH_4^+/g), q_e is the amount of ammonium released at equilibrium, and k_1, k_2, α, β, a, and b are constants. R^2 and SEE for the different models were determined, and a lower SEE value and higher R^2 value were considered to represent goodness of conformity between the measured and estimated NH_4^+ released data.

3. Results and discussion

3.1. NH_4^+ removal process

3.1.1. Removal efficiency

The amounts of ammonium removed by natural Iranian clinoptilolite of millimeter and nanometer particle sizes from aqueous solutions in the presence of Na^+ at different initial NH_4^+ concentrations were determined (Fig. 3). All the data reported are the average values derived from triplicate samples. Based on this analysis, the initial NH_4^+ concentration was found to be an important factor for NH_4^+ removal by zeolite. As the initial concentration of NH_4^+ increased, the removal efficiency of NH_4^+ ion decreased (Fig. 3). This result may be attributed to the ion-exchanger tending to become saturated, resulting in an increase

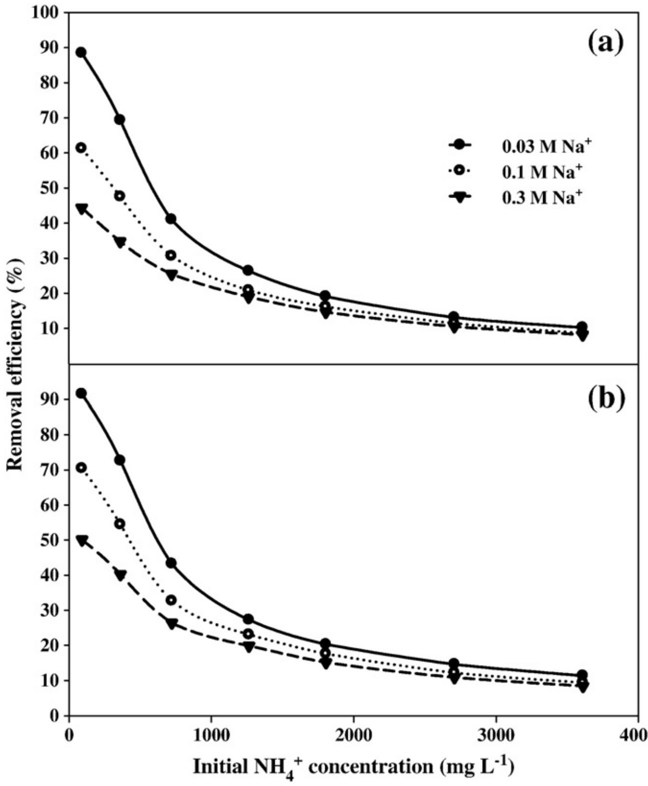


Fig. 3. NH_4^+ removal efficiency of different Na^+ concentrations by Iranian zeolite with millimeter (a) and nanometer (b) particle sizes.

in the driving force required for further exchange of NH_4^+ ions onto the zeolite (Huang et al., 2010).

The millimeter-sized zeolite showed 10.23% to 88.42%, 8.66% to 61.26%, and 8.16% to 44.34% NH_4^+ removal efficiency at Na^+ concentrations of 0.03, 0.1, and 0.3 M, respectively, over a wide range of initial NH_4^+ concentrations (90 to 3620 mg L^{-1}). For the nanometer-sized zeolite, the removal efficiency values were 11.39% to 91.50%, 9.40% to 70.46%, and 8.44% to 50.14% at the three Na^+ concentrations (Fig. 3). This reveals that the NH_4^+ removal efficiency increased with a decrease in particle size, and was likely due to a greater available surface area on the smaller sized particles of clinoptilolite (Wang et al., 2006). As shown in Fig. 3, with an increased Na^+ concentration in the solution, a significant reduction in the NH_4^+ removal occurred due to the competitive effect of Na^+. This reduction was more significant at lower initial NH_4^+ concentrations (Fig. 3).

3.1.2. Ammonium exchange isotherms

Ion-exchange isotherms characterize the equilibrium relationship between the amounts of exchanged ion by zeolite and its equilibrium concentration in the solution (Sarioglu, 2005). In this study, the ion-exchange isotherm data obtained for millimeter- and nanometer-sized zeolite in the presence of Na^+ were fitted to the Freundlich, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models. The resulting exchange isotherms as well as experimental data are shown in Fig. 4. The estimated model parameters, including R^2 and the SEE, for the different models are presented in Table 1, which indicates that the experimental data of NH_4^+ exchange could be well fitted by all four models. It was also made clear that the three-parameter models (Redlich–Peterson, and Langmuir–Freundlich) provided better fitting in terms of R^2 and SEE for all treatments compared to two-parameter isotherms (Freundlich and Langmuir), a result that is supported by the findings of Lei et al. (2008). In practice, however, two-parameter equations are more widely used than three parameter equations due to the inconvenience of evaluating three isotherm parameters. For two-parameter isotherms, the Langmuir model provided a more consistent fit to the experimental data compared with the Freundlich model (Table 1).

Table 1
Isotherm constants and statistical comparison values for NH_4^+ exchange from solutions with Na^+ concentrations of 0.03, 0.1, and 0.3 M on millimeter- and nanometer-sized Iranian zeolite particles.

Model	Millimeter-sized			Nanometer-sized		
	0.03 M	0.1 M	0.3 M	0.03 M	0.1 M	0.3 M
Freundlich						
K	2.73	1.16	0.61	2.81	1.48	0.76
$1/n$	0.18	0.27	0.34	0.19	0.25	0.32
R^2	0.894	0.930	0.995	0.931	0.929	0.945
SEE	1.092	0.824	0.744	0.988	0.878	0.748
Langmuir						
q_m (mg g^{-1})	10.67	9.81	9.93	11.52	10.34	9.92
b (L mg^{-1})	0.022	0.005	0.003	0.022	0.007	0.003
R^2	0.982	0.991	0.999	0.957	0.978	0.992
SEE	0.474	0.304	0.100	0.823	0.494	0.277
Redlich–Peterson						
a	0.35	0.07	0.03	0.57	0.11	0.04
b	0.054	0.013	0.003	0.104	0.023	0.008
n	0.94	0.92	0.98	0.90	0.90	0.92
R^2	0.997	0.996	0.999	0.995	0.991	0.995
SEE	0.173	0.197	0.096	0.256	0.315	0.222
Langmuir–Freundlich						
q_m (mg g^{-1})	11.31	10.50	10.16	13.27	11.48	10.64
b (L mg^{-1})	0.051	0.011	0.003	0.082	0.021	0.006
$1/n$	0.74	0.82	0.95	0.58	0.74	0.85
R^2	0.992	0.994	0.999	0.984	0.988	0.995
SEE	0.299	0.223	0.0864	0.471	0.354	0.223

The dimensionless parameter or separation factor, R_L, based on the further analysis of the Langmuir equation can be given by (Saltali et al., 2007):

$$R_L = \frac{1}{1 + bC_0} \tag{12}$$

Where C_0 (mg L^{-1}) is the initial concentration of exchangeable ion and b is the Langmuir constant. The R_L parameter is considered as more reliable indicator of exchange. There are four probabilities for the R_L value: (i) for favorable exchange, $0 < R_L < 1$, (ii) for unfavorable

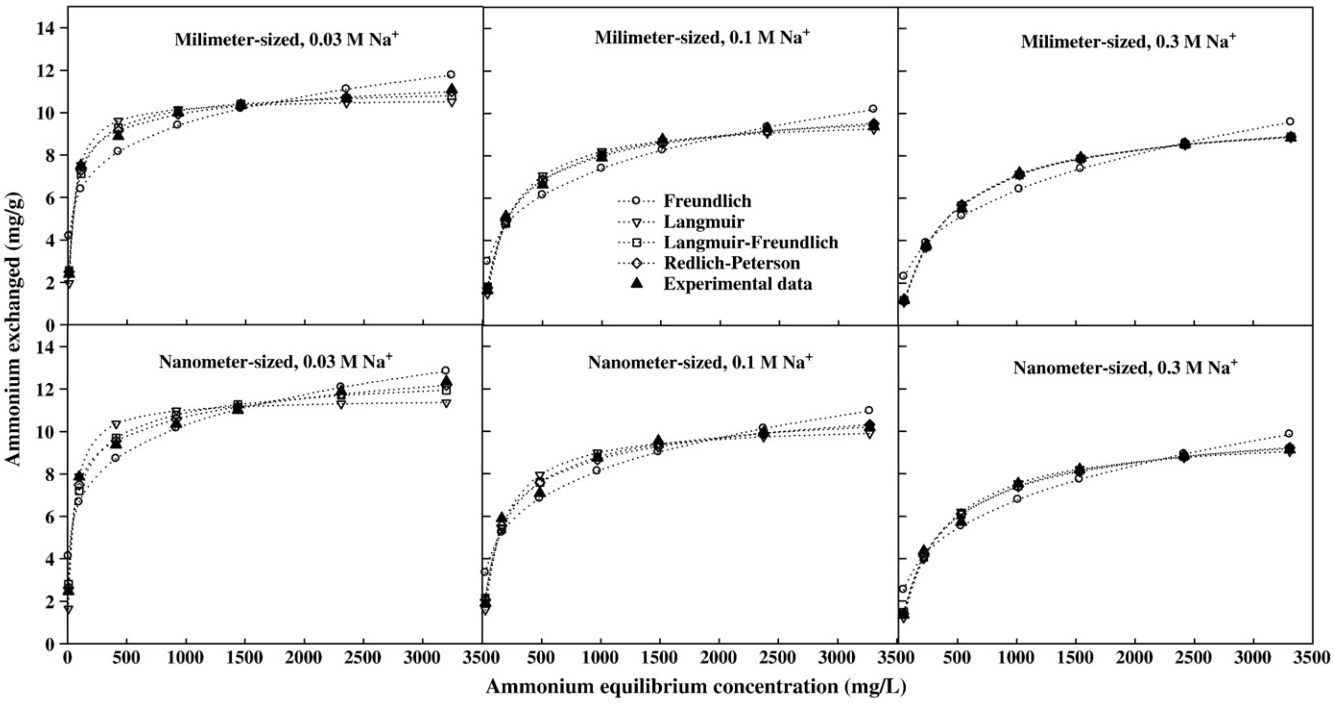


Fig. 4. NH_4^+ exchange isotherms of different Na^+ concentrations by Iranian zeolite with millimeter and nanometer particle sizes.

exchange, $R_L>1$, (iii) for linear exchange, $R_L=1$, and (iv) for irreversible exchange, $R_L=0$ (Gupta and Bhattacharyya, 2005; Hall et al., 1966; Ho, 2003; Ho et al., 2002). Fig. 5 illustrates the variation of R_L with initial concentration of the NH_4^+ ion for all treatments. As can be seen from the curves, the R_L parameters lie between 0 and 1 which indicates that the removal of NH_4^+ ions by the natural Iranian zeolite is propitious. The R_L value obtained in this study also proves that natural zeolite is a potential ion-exchanger for NH_4^+ ion removal from aqueous solutions, which is supported by several previous studies (Karadag et al., 2006; Saltali et al., 2007). Fig. 5 also shows that the R_L value approaches zero as the C_0 value is increased, which indicates that the exchange of NH_4^+ ion onto natural zeolites is less favorable at high concentrations of NH_4^+ (Saltali et al., 2007).

Another parameter, q_m, used in either the Langmuir or Langmuir–Freundlich equations, represents the NH_4^+ ion-exchange capacity (Lei et al., 2008) and is presented in Table 1 for millimeter- and nanometer-sized zeolite and different Na^+ concentrations. It is believed that q_m obtained from the Langmuir–Freundlich equation can be more reasonable than from the Langmuir equation (Lei et al., 2008). The comparison of q_m for millimeter- and nanometer-size zeolite suggests that the maximum NH_4^+ exchange increases with decreasing particle size (Table 1), a result that is consistent with Wang et al., 2006. In addition, at an identical clinoptilolite particle size, the value of q_m varied with the concentration of Na^+ present in the solution. The maximum NH_4^+ exchange capacity by the zeolite at equilibrium was happened in 0.03 M Na^+ which was 11.31 and 13.27 $mgNH_4^+/g$ for millimeter- and nanometer-sized zeolite, respectively (Table 1). The NH_4^+ exchange capacity of previously reported some of the other natural zeolite together with capacities of the present samples (Table 2), indicate that natural Iranian zeolite exhibits a reasonable exchange capacity for NH_4^+.

The *1/n* constant for the Freundlich isotherm ranges from 0 to 1 and is a measure of exchange intensity or surface heterogeneity, with a value of *1/n* smaller than 1 describing a favorable removal conditions (Raji and Anirudhan, 1998). In this study, the value of *1/n* (Freundlich constant) for natural Iranian zeolite was between 0.18 and 0.34 (Table 1), which suggests that the exchange conditions were indeed favorable.

Table 2
NH_4^+-exchange capacities of different zeolites.

Ion exchanger	q_m ($mgNH_4^+/g$) (cmol kg^{-1} in parenthesis)	Source
Natural Hungarian zeolite	11.72 (64.93)	(Hlavay et al., 1982)
New Zealand zeolite	7.39–7.43 (40.94–41.16)	(Nguyen and Tanner, 1998)
Natural Chinese clinoptilolite	14.42 (79.89)	(Wang et al., 2006)
Natural Turkish clinoptilolite	8.12 (44.99)	(Karadag et al., 2006)
Natural Akita clinoptilolite	16.06 (88.98)	(Jha and Hayashi, 2009)
Natural Iranian zeolite (millimeter)	11.31(62.66)	This study
Natural Iranian zeolite (nanometer)	13.27 (73.52)	This study

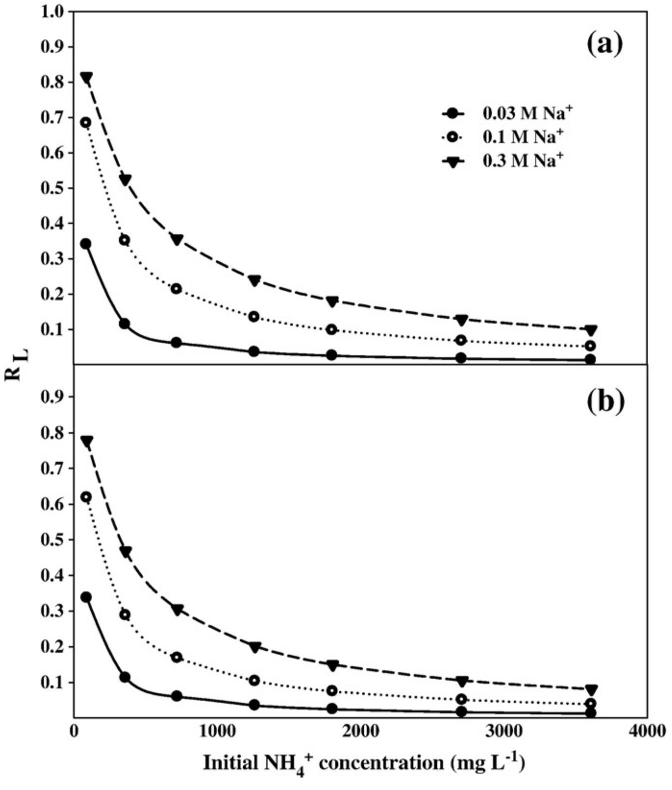


Fig. 5. Variation of separation factor (R_L) as a function of initial NH_4^+ concentration for Na^+ concentrations of 0.03, 0.1, and 0.3 M and zeolite particles of millimeter (a) and nanometer (b) sizes.

3.2. Ammonium release process

3.2.1. Kinetics of NH_4^+ release

The results of the ammonium release kinetic experiments of NH_4^+-loaded Iranian clinoptilolite with millimeter particle size at different ionic strengths are presented in Fig. 6. The NH_4^+ release process was nearly complete within 150–200 min. NH_4^+ release was rapid for the first 60 min, then slower for the rest of the time at all ionic strengths (Fig. 6). Such biphasic release is characteristic of a diffusion-controlled process and has previously been observed for NH_4^+ (Kithome et al., 1998; Steffens and Sparks, 1997) and other similar ions such as K^+ (Feigenbaum et al., 1981; Martin and Sparks, 1983).

It was also observed that the amount of NH_4^+ released increased with increasing ionic strength values (Fig. 6). This was due to the background electrode Na^+ competing with NH_4^+ for exchange sites, resulting in increased NH_4^+ release. For instance, NH_4^+ release in 0.3 M Na^+ was approximately two-fold greater than NH_4^+ release in 0.03 M Na^+, and the NH_4^+ release of deionized water was negligible when compared with releasing solutions with ionic strengths of 0.03, 0.1, and 0.3 M NaCl (Fig. 6).

3.2.2. Conformity of NH_4^+ release data to kinetic models

Several different kinetic models were employed to describe NH_4^+ release from the NH_4^+-loaded Iranian clinoptilolite. The lower SEE (0.043–0.194) and higher R^2 (0.866–0.958) values obtained with the Elovich model suggest that at all ionic strengths the release kinetics were best fitted to this model (Table 3). Aharoni and Sparks (1991)

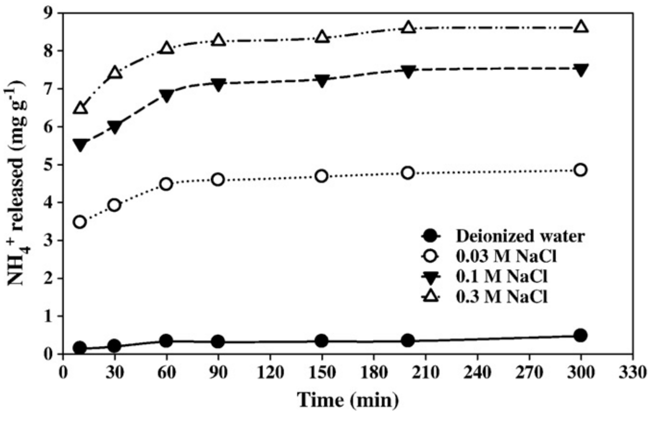


Fig. 6. Ammonium release kinetics by Iranian zeolite of millimeter particle size for different ionic strengths.

Table 3
Kinetic models for NH_4^+ release from Iranian zeolite at different ionic strengths of 0.03, 0.1, and 0.3 M NaCl, as well as deionized water (DW).

Model	DW	0.03	0.1	0.3
Pseudo first-order				
k_1	0.004	0.014	0.018	0.021
R^2	0.829	0.953	0.985	0.979
SEE	0.172	1.843	2.502	2.782
Pseudo second order				
k_2	0.050	0.033	0.020	0.024
R^2	0.842	0.944	0.899	0.970
SEE	0.052	0.237	0.477	0.331
Power function				
a	0.077	2.873	4.526	5.583
b	0.306	0.098	0.094	0.081
R^2	0.873	0.932	0.947	0.929
SEE	0.042	0.145	0.192	0.227
Elovich				
$(1/\beta)\ln(\alpha\beta)$	−0.061	2.570	4.100	5.180
$1/\beta$	0.084	0.420	0.632	0.641
R^2	0.866	0.951	0.958	0.948
SEE	0.043	0.123	0.172	0.194

and Aharoni et al. (1991) have noted that conformity of experimental data to the Elovich equation could suggest a heterogeneous diffusion process (Aharoni and Sparks, 1991; Aharoni et al., 1991). Heterogeneous diffusion can be expressed as (Steffens and Sparks, 1997):

$$d(q\,/\,q_\infty)\,/\,d\ln t = 1\,/\,\rho \tag{13}$$

Where $\rho = \ln(\tau_m/\tau_i)$; τ_i is the smallest τ and τ_m is the largest τ; $\tau = r^2/D$, where r is the maximum length of the diffusion path and D is the diffusion coefficient; q_∞ is the quantity of NH_4^+ released at time t and q is the NH_4^+ released at a certain time (Aharoni and Sparks, 1991; Aharoni et al., 1991). Aharoni and Sparks (1991) predicted that a slope of <0.24 for the relationship $d(q/q_\infty)$ vs. ln t would be expected for heterogeneous diffusion. Fig. 7 shows plots of q/q_∞ vs. ln t for a release process which is nearly linear (R^2 values ranged from 0.866 to 0.958) at all ionic strengths. The slopes of these plots were 0.178, 0.087, 0.084, and 0.075 for DW, 0.03 M NaCl, 0.1 M NaCl, and 0.3 M NaCl, respectively, suggesting heterogeneous diffusion.

Among the models examined, the higher SEE values obtained for the pseudo first-order model varied between 0.172 and 2.782 (Table 3). The possibility of first-order reactions corresponding to multiple independent retention sites in the zeolite mineral was also not justified by the data obtained by Kithome et al. (1998). The pseudo-second order kinetic model provided a better description of NH_4^+ release by the natural clinoptilolite, with SEE and R^2 values ranging from 0.052 to 0.331 and 0.842 to 0.970, respectively (Table 3). The value of the pseudo-second order rate constant (k_2) decreased with increasing ionic strength, as shown by the data in Table 3. This indicates that a solution with a higher ionic strength is likely to reach equilibrium in a shorter time period than one with a lower ionic strength.

The Power function model satisfactorily describes the NH_4^+ release by the natural clinoptilolite with SEE and R^2 values ranging from 0.042 to 0.227 and 0.873 to 0.947, respectively (Table 3). As a represents the initial rate of release, it is clear that the initial release rate of clinoptilolite increases with an increase in the ionic strength (Table 3).

4. Conclusion

In this study, the examined experimental parameters, such as initial NH_4^+ concentration, solution Na^+ concentration, and zeolite particle size, influenced the removal of NH_4^+ ion by zeolite. The NH_4^+ ion-exchange capacity of natural zeolite increased with decreasing particle size and Na^+ concentration, and the NH_4^+ ion exchange data was fitted to the Freundlich, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models. In addition, an increase in ionic strength resulted in greater amounts of NH_4^+ being released. Conformity of the NH_4^+ release data to the Elovich model suggests that the rates of NH_4^+ exchange were governed by a heterogeneous diffusion process. Based on the results, it can be concluded that natural Iranian zeolite is a suitable ion-exchanger for NH_4^+ ion removal and consequently has potential as a controlled-release NH_4^+ fertilizer. As such, it can be recommended for use in wastewater

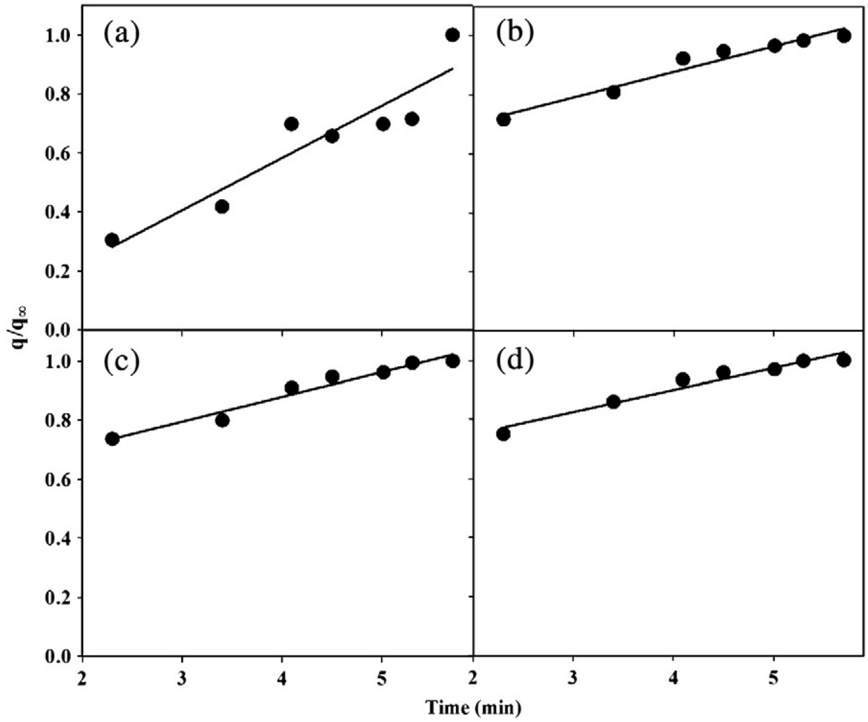


Fig. 7. NH_4^+ release data applied to a heterogeneous diffusion model for (a) deionized water, (b) 0.03 M NaCl, (c) 0.1 M NaCl, and (d) 0.3 M NaCl.

treatment and agriculture purposes as it represents a sustainable, environmentally friendly, and affordable ion exchange material.

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References

Aharoni, C., Sparks, D.L., 1991. Kinetics of soil chemical reactions—a theoretical treatment. In: Sparks, D.L., Suarez, D.L. (Eds.), Rates of Soil Chemical Processes. SSSA Spec. Publ, pp. 1–18.

Aharoni, C., Sparks, D.L., Levinson, S., Ravina, I., 1991. Kinetics of soil chemical reactions: relationships between empirical equations and diffusion models. Soil Sci. Soc. Am. J. 55, 1307–1312.

Allen, E.R., Hossner, L.R., Ming, D.W., Henninger, D.L., 1996. Release rates of phosphorus, ammonium, and potassium in clinoptilolite–phosphate rock systems. Soil Sci. Soc. Am. J. 60, 1467–1472.

Boettinger, J.L., Ming, D.W., 2002. Zeolites. In: Dixon, J.B., Schulze, D.G. (Eds.), Soil Mineralogy with Environmental Applications. SSSA, Madison, Wisconsin, pp. 585–610.

Cassman, K.G., Dobermann, A., Walters, D.T., 2002. Agroecosystems, nitrogen-use efficiency, and nitrogen management. Ambio 31, 132–140.

Chapman, H.D., 1965. Cation exchange capacity. In: Black, C.A. (Ed.), Method of Soil Analysis. SSSA, Madison, pp. 891–901.

Chlopecka, A., Adriano, D.C., 1997. Influence of zeolite, apatite and Fe-oxide on Cd and Pb uptake by crops. Sci. Total Environ. 207, 195–206.

Dimova, G., Mihailov, G., Tzankov, T., 1999. Combined filter for ammonia removal—Part I: Minimal zeolite contact time and requirements for desorption. Water Sci. Technol. 39, 123–129.

Dixon, J.B., Weed, S.B., 1989. Mineral Soil Environment. SSSA, Madison, Wisconsin.

Dwairi, I.M., 1998. Evaluation of Jordanian zeolite tuff as a controlled slow-release fertilizer for NH$_4^+$. Environ. Geol. 34, 1–4.

Feigenbaum, S., Edelstein, R., Shainberg, I., 1981. Release rate of potassium andstructural cations from Micas to ion exchangers in dilute solutions. Soil Sci. Soc. Am. J. 45, 501–506.

Gupta, S.S., Bhattacharyya, K.G., 2005. Interaction of metal ions with clays: I. A case study with Pb(II). Appl. Clay Sci. 30, 199–208.

Hall, K.R., Eagleton, L.C., Acrivos, A., Vermeule, T., 1966. Pore and solid diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fundam. 5, 212–223.

He, Z.L., Calvert, D.V., Alva, A.K., Li, Y.C., Banks, D.J., 2002. Clinoptilolite zeolite and cellulose amendments to reduce ammonia volatilization in a calcareous sandy soil. Plant Soil 247, 253–260.

Hlavay, J., Vigh, G., Olaszi, V., Inczedy, J., 1982. Investigations on natural Hungarian zeolite for ammonia removal. Water Res. 16, 417–420.

Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. Water Res. 37, 2323–2330.

Ho, Y.S., Huang, C.T., Huang, H.W., 2002. Equilibrium sorption isotherm for metal ions on tree fern. Process Biochem. 37, 1421–1430.

Huang, H.M., Xiao, X.M., Yan, B., Yang, L.P., 2010. Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. J. Hazard. Mater. 175, 247–252.

Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P., 2002. Equilibrium and kinetic ion exchange studies of Pb^{2+}, Cr^{3+}, Fe^{3+} and Cu^{2+} on natural clinoptilolite. Water Res. 36, 2784–2792.

Jha, V.K., Hayashi, S., 2009. Modification on natural clinoptilolite zeolite for its NH$_4^+$ retention capacity. J. Hazard. Mater. 169, 29–35.

Karadag, D., Koc, Y., Turan, M., Armagan, B., 2006. Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. J. Hazard. Mater. 136, 604–609.

Kazemian, H., 2002. Zeolite science in Iran: a brief review. Zeolite 02. 6th International Conference Occurrence, Properties and Utilization of Natural Zeolite, Thessaloniki, Greece, pp. 162–163.

Keeney, D.R., Nelson, D.W., 1982. Nitrogen inorganic forms, In: Page, A.L. (Ed.), Methods of Soil Analysis, Part 2, second ed. SSSA. Madison, Agronomy ASA, pp. 643–698.

Kithome, M., Paul, J.W., Lavkulich, L.M., Bomke, A.A., 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. Soil Sci. Soc. Am. J. 62, 622–629.

Kumar, K.V., Sivanesan, S., 2006. Pseudo second order kinetic models for safranin onto rice husk: comparison of linear and non-linear regression analysis. Process Biochem. 41, 1198–1202.

Kurama, H., Zimmer, A., Reschetilowski, T., 2002. Chemical modification effect on the sorption capacities of natural clinoptilolite. Chem. Eng. Technol. 25, 301–305.

Lei, L.C., Li, X.J., Zhang, X.W., 2008. Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite. Sep. Purif. Technol. 58, 359–366.

Maranon, E., Ulmanu, M., Fernandez, Y., Anger, I., Castrillon, L., 2006. Removal of ammonium from aqueous solutions with volcanic tuff. J. Hazard. Mater. 137, 1402–1409.

Martin, H.W., Sparks, D.L., 1983. Kinetics of nonexchangeable potassium release from two coastal plain soils. Soil Sci. Soc. Am. J. 47, 883–887.

Nguyen, M.L., Tanner, C.C., 1998. Ammonium removal from wastewaters using natural New Zealand zeolites. New Zeal. J. Agr. Res. 41, 427–446.

Owens, L.B., Edwards, W.M., Vankeuren, R.W., 1992. Nitrate levels in shallow groundwater under pastures receiving ammonium nitrate or slow-release nitrogen fertilizer. J. Environ. Qual. 21, 607–613.

Park, M., Komarneni, S., 1998. Ammonium nitrate occlusion vs. nitrate ion exchange in natural zeolites. Soil Sci. Soc. Am. J. 62, 1455–1459.

Raji, C., Anirudhan, T.S., 1998. Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. Water Res. 32, 3772–3780.

Rehakova, M., Cuvanova, S., Dzivak, M., Rimar, J., Gaval'ova, Z., 2004. Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. Curr. Opin. Solid State Mater. Sci. 8, 397–404.

Saltali, K., Sari, A., Aydin, M., 2007. Removal of ammonium ion from aqueous solution by natural Turkish (YIldIzeli) zeolite for environmental quality. J. Hazard. Mater. 141, 258–263.

Sarioglu, M., 2005. Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. Sep. Purif. Technol. 41, 1–11.

Shirvani, M., Shariatmadari, H., Kalbasi, M., 2007. Kinetics of cadmium desorption from fibrous silicate clay minerals: Influence of organic ligands and aging. Appl. Clay Sci. 37, 175–184.

Steffens, D., Sparks, D.L., 1997. Kinetics of nonexchangeable ammonium release from soils. Soil Sci. Soc. Am. J. 61, 455–462.

Wang, Y.Q., Liu, S.J., Xu, Z., Han, T.W., Chuan, S., Zhu, T., 2006. Ammonia removal from leachate solution using natural Chinese clinoptilolite. J. Hazard. Mater. 136, 735–740.

Willmott, C.J., 1982. Some comments on the evaluation of model performance. B. Am. Meteorol. Soc. 63, 1309–1313.