

Kinetics of Ammonium Adsorption and Desorption by the Natural Zeolite Clinoptilolite

M. Kithome, J. W. Paul,* L. M. Lavkulich, and A. A. Bomke

ABSTRACT

The kinetics of NH_4^+ adsorption and desorption were investigated on the natural zeolite clinoptilolite to ascertain its ability to adsorb and release the important plant nutrient N in its NH_4^+ form at various pH values and initial NH_4^+ concentrations. Kinetics of NH_4^+ adsorption were evaluated on the samples using solutions containing 140.1, 280.2, 560.4, and 840.6 mg L^{-1} of NH_4^+ -N at pH 4, 5, 6, and 7, equilibrated for 5, 10, 15, 20, 30, 45, 60, 75, 90, and 120 min. Samples for NH_4^+ desorption were equilibrated with 70.1, 280.2, 560.4, and 1401 mg L^{-1} NH_4^+ -N solution at pH 4, 5, 6, and 7 for 2.5 h, and adsorbed NH_4^+ extracted with 2 M KCl for 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, and 300 min. Equilibrium time for NH_4^+ adsorption ranged from 60 min for 140.1 mg L^{-1} initial NH_4^+ -N concentration at pH 4 to 120 min for 840.6 mg L^{-1} initial NH_4^+ -N concentration at pH 7. Desorption was nearly complete in 150 min for low initial NH_4^+ concentrations and 200 min for high initial NH_4^+ concentrations. Amounts of NH_4^+ sorbed increased with increasing pH and initial NH_4^+ concentrations. Models evaluated included the first-order kinetics, modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion. All the models adequately described the NH_4^+ adsorption process, with r^2 values ranging from 0.955 to 0.999. With the exception of first-order kinetics, they also described the desorption process well, with r^2 values ranging from 0.897 to 0.999, for all pH and initial NH_4^+ concentrations. Reaction rate coefficients (k) were calculated from the modified Freundlich model and ranged from 0.134 to 0.193 min^{-1} for the adsorption process, and 0.129 to 0.226 min^{-1} for the desorption process. The models indicated that NH_4^+ adsorption and desorption by the zeolite was diffusion controlled. Data from this study indicated the potential use of the tested natural zeolite as an NH_4^+ adsorbent and a controlled-release NH_4^+ fertilizer.

ZEOLITES are naturally occurring framework aluminosilicate minerals with high cation-exchange capacity, ion adsorption, and high NH_4^+ -selective properties. More than 50 different species of this mineral group have been identified (Tsitsishvili et al., 1992), among them clinoptilolite with the formula



Clinoptilolite is an abundant natural zeolite found in igneous, sedimentary, and metamorphic deposits, and has a high cation-exchange capacity (CEC) and affinity for NH_4^+ . The framework structure of clinoptilolite consists of interlinked four- and five-tetrahedral rings, creating a layer. Between these layers are open eight- and 10-tetrahedral ring channels having approximate dimensions of 7.9×10^{-8} by 3.5×10^{-8} m and 4.4×10^{-8} by 3.0×10^{-8} m, respectively (Vaughan, 1978). These rings form the ion sieving channels in clinoptilolite (Breck,

1974). Several cation selectivity series have been documented for clinoptilolite. Howery and Thomas (1965) found NaCl-treated clinoptilolite to have a $\text{Cs} > \text{NH}_4^+ \gg \text{Na}$ selectivity sequence. Ames (1967) reported the following selectivity sequence for the removal of ions from simulated wastewater by clinoptilolite: $\text{K} > \text{NH}_4^+ > \text{Na} > \text{Ca}, \text{Mg}$.

The high affinity of zeolites for NH_4^+ and the possibility of releasing it over time is of special interest for minimizing environmental pollution during animal waste management. The NH_4^+ adsorption properties of zeolites have enabled them to be used as NH_4^+ and/or NH_3 adsorbents during composting (Bernal et al., 1993) and in poultry facilities (Koelliker et al., 1978), whereas their ability to desorb the adsorbed NH_4^+ ions gives them the potential to be used as controlled-release NH_4^+ fertilizers. For adsorbents to be effective in increasing N-use efficiency, they must be able to trap large amounts of NH_4^+ and release this N slowly during the growing season when applied to soil (Johnson et al., 1983). Rapid release of the adsorbed NH_4^+ would increase the potential for N loss when applied to soil, and too slow a rate of release would limit the short-term benefits to the crop.

Equilibrium reactions between solution and exchangeable phases of zeolite- NH_4^+ profoundly influence the chemistry of NH_4^+ adsorption and desorption by zeolites. Understanding the kinetics of the adsorption and desorption processes in natural zeolites is necessary for effective utilization of natural zeolites as NH_3 and NH_4^+ adsorbents, and consequently as controlled-release NH_4^+ fertilizers.

Several models have been used to describe adsorption and desorption of ions from soils and soil minerals. First-order kinetic models have been applied extensively to cation and anion sorption in soils. Sawhney (1966) described the uptake of Cs on vermiculitic clay minerals as a pseudo-first-order rate reaction. Carski and Sparks (1987) described NH_4^+ release from soils using a first-order kinetic model. Kuo and Lotse (1974) proposed a modification of the Freundlich model to describe the kinetics of phosphate adsorption and desorption by hematite and gibbsite, and Sparks et al. (1980) used this model to study the kinetics of K adsorption from solution to exchangeable phases for two soils. The parabolic-diffusion model has been used by many researchers to describe diffusion-controlled phenomena in soil constituents and release of ions in soils and soil minerals (Cooke, 1966; Evans and Jurinak, 1976; Feigenbaum et al., 1981; Havlin et al., 1985). The exponential Elovich model, which has general application to chemisorption kinetics (Low, 1960), has been used to describe the kinetics of ion adsorption and desorption on soils and

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soil minerals (Chien and Clayton, 1980; Sparks and Jardine, 1984; Peryea et al., 1985). Recently, Steffens and Sparks (1997) used, among others, the heterogeneous diffusion model to describe the kinetics of nonexchangeable NH_4^+ release from soils.

Ammonium adsorption and desorption by zeolites in NH_4^+ -aqueous systems is driven by cation-exchange reactions. Equilibrium relationships in these systems have been investigated (Weber et al., 1983; Bernal and Lopez-Real, 1993), but the kinetics of adsorption and desorption processes in these systems have not been studied. The objectives of this study were to determine the time, pH, and initial concentration dependencies of NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite, and identify empirical models that best describe the adsorption and desorption processes.

MATERIALS AND METHODS

Zeolite Sample

A natural zeolite mined in the southwestern USA and supplied by Aberhill's Holdings Inc.¹, Abbotsford, BC, Canada, was used in this study. The sample was air dried and ground to <2 mm. Mineral identification using x-ray diffraction showed that the zeolite consisted mainly of clinoptilolite, with traces of quartz and feldspar. Some of its physical and chemical characteristics are listed in Table 1. The pH was determined in a 1:2 zeolite/water or 1 M KCl suspensions. Electrical conductivity was measured in a 1:2 zeolite/water extract. A simplified ethylene glycol monoethyl ether procedure was used to determine the specific surface area (Cihacek and Bremner, 1979). Ammonium N was extracted with 2 M KCl and determined spectrophotometrically using an automated continuous-flow injection analyzer. The neutral 1 M NH_4OAc saturation procedure was used for determining the CEC (Chapman, 1965). Exchangeable cations were analyzed from the NH_4OAc extract by atomic absorption spectrometry. Total C was determined using a Leco carbon analyzer (Leco Corp., St. Joseph, MI).

Kinetics of Ammonium Adsorption

We studied the kinetics of NH_4^+ adsorption at four pH levels, four initial NH_4^+ -N concentrations, and 10 agitation times, with all the treatments replicated three times. We weighed 0.5-g zeolite samples in 50-mL polypropylene centrifuge tubes, and added 5 mL of NaOAc-HOAc buffer solution at pH 4, 5, 6, and 7 followed by 10 mL of NH_4Cl solution containing 140.1, 280.2, 560.4, and 840.6 mg NH_4^+ -N L^{-1} . We used isonormal solutions of $\text{NH}_4\text{Cl} + \text{NaCl}$ (total 0.2 M) to maintain a constant ionic strength in the sample solution mixtures and to provide competing ions for exchange sites (Weber et al., 1983; Bernal and Lopez-Real, 1993). The centrifuge tubes were laid horizontally on a reciprocating shaker and agitated continuously at 22°C for 5, 10, 15, 20, 30, 45, 60, 75, 90, and 120 min at 240 cycles min^{-1} followed by centrifugation at 2000 × *g* relative centrifugal force (RCF) for 10 min. Ammonium in the supernatant was analyzed spectrophotometrically using an automated continuous-flow injection analyzer. Amounts of NH_4^+ sorbed by the samples were calculated from the reduction of NH_4^+ in the solution.

¹ Trade names and company names are included for the benefit of the reader and do not imply endorsement or preferential treatment of the product listed as "natural zeolite".

Table 1. Some characteristics of the zeolite sample.

pH (H ₂ O)	7.87
pH (KCl)	5.84
Surface area, m ² kg ⁻¹	9.35 × 10 ⁵
Electrical conductivity, S m ⁻¹	0.17
Total C, mg kg ⁻¹	0.00
NH_4^+ -N, mg kg ⁻¹	12.30
Cation-exchange capacity, cmol _c kg ⁻¹	92.78
Exchangeable cations, cmol kg ⁻¹	
Na ⁺	3.07
K ⁺	10.40
Ca ²⁺	44.79
Mg ²⁺	7.78

Kinetics of Ammonium Desorption

We conducted desorption studies at four pH levels, four initial NH_4^+ -N concentrations, and 11 agitation times, with all the treatments replicated three times. We weighed 0.5-g zeolite samples in 50-mL polypropylene centrifuge tubes, and added 5 mL of HOAc-NaOAc buffer solution at pH 4, 5, 6, and 7, followed by 10 mL of 70.1, 280.2, 560.4, and 1401 mg L^{-1} of NH_4^+ -N solution. Isonormal solutions of $\text{NH}_4\text{Cl} + \text{NaCl}$ (total 0.2 M) were used. The centrifuge tubes were agitated continuously on a reciprocating shaker at 22°C for 2.5 h, followed by centrifugation at 2000 × *g* RCF for 10 min. The supernatant was analyzed for NH_4^+ using an automated continuous-flow injection analyzer. We calculated the amounts of NH_4^+ on the exchange sites of the zeolite samples at zero time of desorption from the reduction of NH_4^+ in the solution. We washed the samples remaining in the centrifuge tubes thoroughly with ethanol and deionized water, and extracted the adsorbed NH_4^+ with 10-mL portions of 2 M KCl by agitating on a reciprocating shaker for 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, and 300 min, followed by centrifugation at 2000 × *g* RCF for 10 min. The supernatant was analyzed for desorbed NH_4^+ at each time of agitation using the automated continuous-flow injection analyzer.

Kinetic Models

Different kinetic models described below were used to describe NH_4^+ adsorption and desorption by the natural zeolite clinoptilolite. The goodness of conformity between experimental data and the model-predicted values was expressed by the coefficient of determination (r^2). A relatively high r^2 value for the relationship between measured and predicted NH_4^+ adsorption or desorption data indicated that the model successfully described the kinetics of NH_4^+ adsorption and desorption by the natural zeolite. It should be noted that a high r^2 value for a particular kinetic model does not necessarily mean that this model is the best (Sparks, 1989). A model also cannot be used to definitively determine the mechanisms of NH_4^+ adsorption or desorption.

First-Order Kinetic Model

The first-order rate model for the adsorption process can be expressed as (Sparks and Jardine, 1981)

$$\log_{10}(1 - F_a) = k't \quad [1]$$

where F_a is the fraction of NH_4^+ adsorbed (X_t/X_{eq}), X_t is the total amount of NH_4^+ adsorbed on the zeolite at time t , X_{eq} is total amount of NH_4^+ adsorbed on the zeolite at equilibrium, k' is the apparent adsorption rate coefficient, defined as $kX_{eq}/2.303$, and k is the absolute velocity coefficient for the adsorption process. If the rate of NH_4^+ adsorption by the zeolite follows first-order kinetics, then a plot of $\log_{10}(1 - F_a)$ against the reaction time t should yield a linear relationship.

For the desorption process, the first-order rate model is expressed as (Sparks and Jardine, 1981)

$$\log_{10}(X_t/X_0) = k_d' t \quad [2]$$

where X_t is the amount of NH_4^+ on the exchange sites of the zeolite at time t of desorption, X_0 is the amount of NH_4^+ on the exchange sites of the zeolite at zero time of desorption, t is the reaction time in minutes, and k_d' is the apparent desorption rate coefficient in 1/minute. This equation is valid if NH_4^+ adsorption is assumed to be negligible. The $\log_{10}(X_t/X_0)$ vs. t relationship is linear if the rate of release of NH_4^+ follows first-order kinetics.

Modified Freundlich Model

The modified Freundlich model as proposed by Kuo and Lotse (1974) is

$$X_t = k C_0 t^{1/m} \quad [3]$$

or

$$\log_{10} X_t = (\log_{10} k + \log_{10} C_0) + 1/m \log_{10} t \quad [4]$$

where X_t is the amount of NH_4^+ -N sorbed at time t per unit weight of zeolite, k is the adsorption or desorption rate coefficient, C_0 is the initial NH_4^+ -N concentration, t is the reaction time, and m is a constant. A plot of $\log_{10} X_t$ vs. $\log_{10} t$ should be linear if the NH_4^+ adsorption or desorption process conforms to the modified Freundlich model.

Parabolic Diffusion Model

The parabolic diffusion model may be stated as follows (Sivasubramanian and Talibudeen, 1972)

$$F = R t^{1/2} + \text{constant} \quad [5]$$

where F is the fraction of NH_4^+ sorbed at time t and R is the overall diffusion constant. Plots of F or the amount of adsorbate (X_t) sorbed at time t against $t^{1/2}$ are often used to test a diffusion-controlled reaction rate (Cooke, 1966; Vaidyanathan and Talibudeen, 1968; Sparks and Jardine, 1984).

Elovich Model

The Elovich equation as modified by Chien and Clayton (1980) was used to study the kinetics of NH_4^+ adsorption and desorption. It is expressed as

$$X_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad [6]$$

where X_t is the amount of NH_4^+ -N (mg kg^{-1}) sorbed at time t , and α and β are constants. If NH_4^+ adsorption or desorption conforms to the Elovich model, a plot of X_t vs. $\ln t$ should yield a linear relationship with a slope of $1/\beta$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The chemical significance of these constants has not been clearly resolved (Sparks, 1989).

Heterogeneous Diffusion Model

The heterogeneous diffusion model can be mathematically expressed as (Aharoni et al., 1991; Aharoni and Sparks, 1991)

$$Z = (dq/dt)^{-1} = \rho t/q_\infty [1 - (4t/\pi\tau_m)^{1/2} - 8/\pi^2 \exp(-\pi^2 t/4\tau_i)]^{-1} \quad [7]$$

where Z is the reciprocal of the rate of NH_4^+ adsorption or desorption; t is time; $\rho = \ln(\tau_m/\tau_i)$ where 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

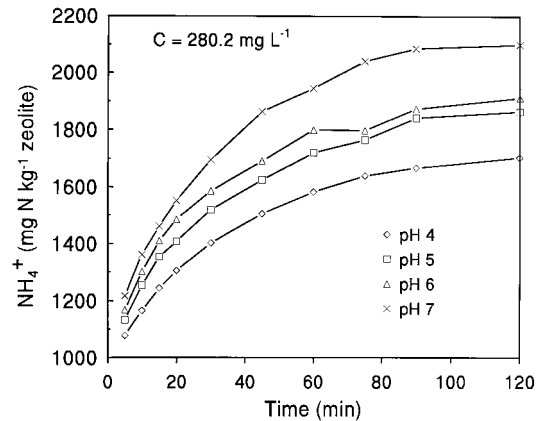


Fig. 1. Ammonium adsorbed by zeolite with time at an initial NH_4^+ -N concentration of 280.2 mg L^{-1} and pH 4, 5, 6, and 7.

the amount of NH_4^+ -N sorbed at 2 or 5 h; and q_∞ is amount of NH_4^+ -N sorbed at time t . In heterogeneous diffusion, a $Z(t)$ plot is mainly linear because the negative terms in Eq. [7] are negligible. Hence Eq. [7] reduces to

$$d(q/q_\infty)/d \ln t = 1/\rho \quad [8]$$

RESULTS AND DISCUSSION

Initial NH_4^+ concentration and pH significantly affected the amount of NH_4^+ adsorbed by the zeolite. An increase in pH resulted in greater amounts of NH_4^+ being adsorbed at any given solution concentration (Fig. 1), probably due to the formation of new sorption sites, together with a decrease in ionic competition for these sites (Garcia-Miragaya and Page, 1976). Also, the amount of NH_4^+ adsorbed increased as the initial NH_4^+ concentration increased, which is expected from a concentration standpoint (Kelly, 1948).

Increasing pH and initial NH_4^+ concentration resulted in greater amounts of NH_4^+ being desorbed, but the fraction of the total adsorbed NH_4^+ that was desorbed decreased. Total NH_4^+ desorbed ranged from 65.2% for high initial NH_4^+ concentration to 89.5% for low initial NH_4^+ concentration at all pH values.

Kinetics of Ammonium Exchange

Adsorption

The NH_4^+ adsorption process was virtually complete in the 140.1 mg NH_4^+ -N L^{-1} treated zeolite samples within 60 min at pH 4 and 80 min at pH 7. The 840.6 mg NH_4^+ -N L^{-1} treated zeolite samples reached equilibrium in approximately 80 min at pH 4 while equilibrium was not reached at pH 7 until about 120 min. These findings are in agreement with those of Weber et al. (1983) and Bernal and Lopez-Real (1993), who observed that sorption of NH_4^+ by natural zeolites was essentially complete after shaking for 1 to 2 h.

Desorption

The kinetics of NH_4^+ desorption by the natural zeolite are shown in Fig. 2 for initial NH_4^+ -N concentration of 280.2 mg L^{-1} , at all pH values. These plots are represen-

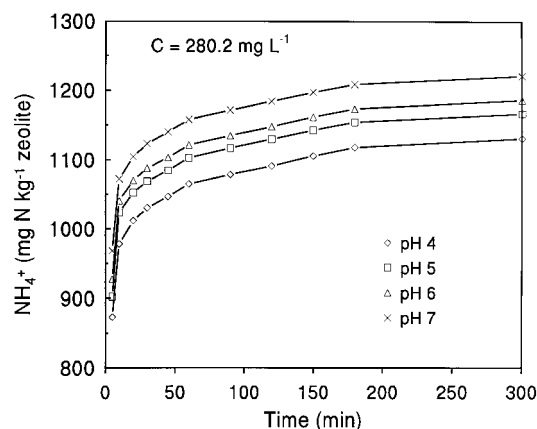


Fig. 2. Cumulative $\text{NH}_4^+\text{-N}$ desorbed by the zeolite with time at an initial $\text{NH}_4^+\text{-N}$ concentration of 280.2 mg L^{-1} and pH 4, 5, 6, and 7.

tative of those found for all the other treatments. The desorption process was nearly complete within 150 to 200 min for both low and high initial NH_4^+ concentrations. The desorption was rapid for the first 20 min, then slower for the rest of the time at all pH values and initial NH_4^+ concentrations. This biphasic desorption is characteristic of a diffusion-controlled process and has previously been observed for NH_4^+ (Steffens and Sparks, 1997) and other similar ions, like K^+ (Feigenbaum et al., 1981; Martin and Sparks, 1983).

Application of Data to Kinetic Models

Adsorption Process

The adsorption data were found to conform to the first-order kinetic model, with r^2 values ranging from 0.961 to 0.999 (Table 2). This was unexpected because several separate reactions may have taken place. This indicated that all reactive sites had similar reaction rates, or offsetting errors resulted in a reasonable average fit of the data, or perhaps some other mechanism was operating that can coincidentally be described by the first-order rate equation. This same equation has been

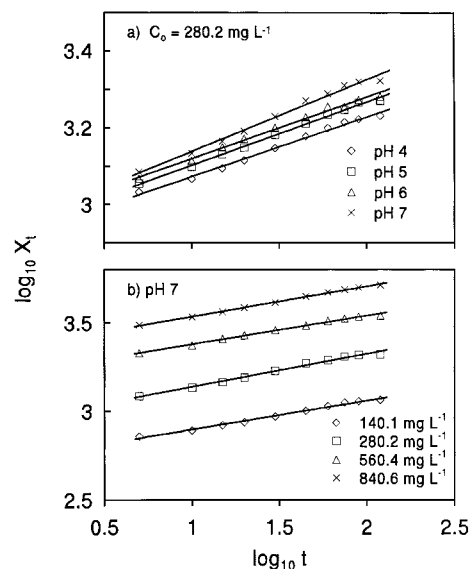


Fig. 3. Relationship between $\text{NH}_4^+\text{-N}$ adsorbed with time as described by the modified Freundlich model for (a) 280.2 mg L^{-1} initial added $\text{NH}_4^+\text{-N}$ concentration for all tested pH values, and (b) all initially added $\text{NH}_4^+\text{-N}$ concentrations at pH 7.

shown to describe both film diffusion-controlled reactions and chemically controlled reactions for isotopic exchange conditions (Boyd et al., 1947). Helfferich (1983) stated that other reactions known to be diffusion controlled can also be described using second-order chemical reactions through a mathematical coincidence. Other information must then be used to determine the rate-limiting mechanism.

Plots of the measured NH_4^+ adsorption data vs. the predicted adsorption data using the modified Freundlich model are shown in Fig. 3 for different pH and initial NH_4^+ concentrations. The r^2 values of this model ranged from 0.983 to 0.998 (Table 3) therefore describing the NH_4^+ adsorption process well. Bache and Williams (1971) indicated that the energy of adsorption decreased exponentially with increasing surface saturation when

Table 2. Regression equations for the first-order kinetic model and correlation coefficients (r^2) for NH_4^+ adsorption and desorption at various pH, initial $\text{NH}_4^+\text{-N}$ concentrations (C_0), and adsorbed $\text{NH}_4^+\text{-N}$ (C^*).

pH	Adsorption			Desorption			
	C_0 mg L ⁻¹	First-order	r^2	C_0 mg L ⁻¹	$C^*\dagger$ mg kg ⁻¹	First-order	r^2
	140.1			70.1			
4		$-0.3994 - 0.0087t$	0.993		542	$-0.4961 - 0.0020t$	0.977
5		$-0.3984 - 0.0087t$	0.990		548	$-0.4868 - 0.0020t$	0.980
6		$-0.3403 - 0.0100t$	0.999		551	$-0.4910 - 0.0019t$	0.981
7		$-0.3707 - 0.0094t$	0.987		562	$-0.5236 - 0.0022t$	0.981
	280.2			280.2			
4		$-0.3954 - 0.0093t$	0.992		1733	$-0.3746 - 0.0005t$	0.903
5		$-0.3666 - 0.0099t$	0.988		1751	$-0.3932 - 0.0005t$	0.917
6		$-0.3948 - 0.0097t$	0.985		1831	$-0.3761 - 0.0004t$	0.912
7		$-0.3560 - 0.0083t$	0.961		1843	$-0.3918 - 0.0004t$	0.900
	560.4			560.4			
4		$-0.3730 - 0.1170t$	0.995		2946	$-0.4874 - 0.0004t$	0.801
5		$-0.3638 - 0.0102t$	0.996		3018	$-0.5374 - 0.0003t$	0.767
6		$-0.3802 - 0.0101t$	0.990		3092	$-0.5328 - 0.0003t$	0.728
7		$-0.3614 - 0.0108t$	0.997		3330	$-0.4773 - 0.0002t$	0.718
	840.6			1401.0			
4		$-0.4835 - 0.0098t$	0.991		5595	$-0.5032 - 0.0002t$	0.663
5		$-0.4986 - 0.0101t$	0.990		5728	$-0.5189 - 0.0002t$	0.733
6		$-0.4355 - 0.0104t$	0.998		5908	$-0.4949 - 0.0002t$	0.646
7		$-0.3454 - 0.0100t$	0.999		5946	$-0.4972 - 0.0001t$	0.734

$\dagger C^*$ is the amount of $\text{NH}_4^+\text{-N}$ on the exchange complex of the zeolite before desorption was initiated.

Table 3. Regression equations and coefficients of determination for NH_4^+ -N adsorption using the modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion models at various pH and initial NH_4^+ -N concentrations (C_0).

C_0 , mg L ⁻¹	pH	Modified Freundlich	r^2	Parabolic diffusion	r^2	Elovich	r^2	Heterogeneous diffusion	r^2
140.1	4	$2.665 + 0.156 \log t$	0.989	$516.3 + 46.5t^{1/2}$	0.967	$386.7 + 120.0 \ln t$	0.989	$0.927 + 0.128 \ln t$	0.988
	5	$2.683 + 0.160 \log t$	0.991	$539.3 + 50.2t^{1/2}$	0.966	$399.5 + 129.3 \ln t$	0.993	$0.928 + 0.131 \ln t$	0.993
	6	$2.695 + 0.167 \log t$	0.994	$550.5 + 55.9t^{1/2}$	0.994	$405.1 + 140.7 \ln t$	0.976	$0.902 + 0.132 \ln t$	0.980
	7	$2.734 + 0.162 \log t$	0.990	$597.8 + 59.0t^{1/2}$	0.995	$439.6 + 150.6 \ln t$	0.981	$0.916 + 0.131 \ln t$	0.976
280.2	4	$2.917 + 0.155 \log t$	0.993	$916.8 + 83.6t^{1/2}$	0.987	$688.1 + 214.5 \ln t$	0.989	$0.922 + 0.127 \ln t$	0.987
	5	$2.937 + 0.165 \log t$	0.996	$964.1 + 95.3t^{1/2}$	0.988	$700.9 + 245.3 \ln t$	0.992	$0.917 + 0.133 \ln t$	0.991
	6	$2.959 + 0.160 \log t$	0.992	$1023 + 94.7t^{1/2}$	0.966	$754.3 + 245.5 \ln t$	0.995	$0.923 + 0.130 \ln t$	0.994
	7	$2.952 + 0.186 \log t$	0.991	$989.4 + 121.7t^{1/2}$	0.986	$668.9 + 307.7 \ln t$	0.987	$0.925 + 0.151 \ln t$	0.988
560.4	4	$3.177 + 0.157 \log t$	0.983	$1615 + 168.5t^{1/2}$	0.972	$1197 + 415.3 \ln t$	0.996	$0.927 + 0.128 \ln t$	0.987
	5	$3.180 + 0.172 \log t$	0.998	$1720 + 171.7t^{1/2}$	0.976	$1222 + 449.9 \ln t$	0.995	$0.936 + 0.137 \ln t$	0.995
	6	$3.200 + 0.165 \log t$	0.996	$1794 + 169.2t^{1/2}$	0.975	$1188 + 473.6 \ln t$	0.997	$0.942 + 0.135 \ln t$	0.989
	7	$3.210 + 0.167 \log t$	0.998	$1837 + 176.7t^{1/2}$	0.981	$1227 + 488.6 \ln t$	0.998	$0.928 + 0.133 \ln t$	0.994
840.6	4	$3.389 + 0.123 \log t$	0.995	$2707 + 174.9t^{1/2}$	0.972	$2199 + 458.7 \ln t$	0.994	$0.937 + 0.106 \ln t$	0.994
	5	$3.400 + 0.123 \log t$	0.991	$2789 + 177.7t^{1/2}$	0.955	$2255 + 471.4 \ln t$	0.998	$0.944 + 0.106 \ln t$	0.998
	6	$3.393 + 0.135 \log t$	0.998	$2752 + 198.9t^{1/2}$	0.977	$2186 + 517.4 \ln t$	0.997	$0.928 + 0.112 \ln t$	0.996
	7	$3.365 + 0.170 \log t$	0.998	$2593 + 265.8t^{1/2}$	0.988	$1840 + 691.2 \ln t$	0.992	$0.906 + 0.134 \ln t$	0.990

the adsorption fitted the Freundlich equation. Interactions between the molecules may explain the decreasing energy of adsorption with increasing surface saturation. Everett (1965) suggested that for adsorbed gas molecules, a decrease in the distance between two adsorbed molecules will increase the perturbation potential. This interaction is also likely to exist between adsorbed NH_4^+ molecules. At low surface saturation, the adsorbed NH_4^+ molecules tend to locate themselves so that they obtain a minimum potential energy. With increasing NH_4^+ adsorption, the distance between the adsorbed NH_4^+ molecules decreases and the perturbation energy as well as the total potential energy of the adsorbed NH_4^+ molecules increases. Thus, the surfaces of the adsorbent may not necessarily contain sites of different energy levels as indicated by Muljadi et al. (1966a,b,c), but may hold the adsorbed molecules at different energy levels because of interactions between the adsorbed molecules. A clear distinction between the adsorbed molecules with respect to their potential energy is not possible.

The parabolic diffusion model also described the NH_4^+ adsorption process well, with r^2 values ranging from 0.955 to 0.995 (Table 3). Conformity to the parabolic diffusion model suggested that the process of NH_4^+ adsorption by the natural zeolite was diffusion controlled, and either intraparticle diffusion or surface diffusion may be rate limiting (Helfferich, 1983; Crank, 1976). The former diffusional process is a transport of the adsorbing ion through the liquid associated with less accessible exchange sites of the adsorbent, whereas the latter involves the movement of the adsorbing ion along the walls of the less accessible spaces of the adsorbent. When particle resistance determines the adsorption velocity, surface diffusion is generally the rate-controlling mechanism (Jardine and Sparks, 1984). Intraparticle surfaces in the natural zeolite clinoptilolite arise from intracrystal spaces within the mineral assemblage and from the network of channels and cages within the crystal structure. Even though zeolites are tectosilicates, the exchange of one counter ion for another of different size could affect the ease of motion for adsorbing ions,

and in so doing lead to variations of the diffusion coefficients as we observed in this study (Table 3).

The experimental data fit the Elovich model successfully, with r^2 values ranging from 0.976 to 0.998 (Table 3). The good fit of this model for the NH_4^+ adsorption data proves its utility for empirical prediction. As noted by Parravano and Boudant (1955), the Elovich model may describe a number of different processes, including bulk and surface diffusion, as well as activation and inactivation of catalytic surfaces. However, prediction is still marginal at very low and very high surface coverages (Ungarish and Aharoni, 1981). Estimated α and β values of the Elovich equation for NH_4^+ sorption by the natural zeolite were found to vary with pH and initial NH_4^+ concentration. Some investigators have used Elovich parameters to estimate reaction rates. Chien and Clayton (1980) suggested that a decrease in β or an increase in α should enhance the reaction rate. This may be questionable because the slope of plots using an equation like Eq. [6] changes with the level of added ion, as was observed in this study, and with the solution/adsorbent ratio (Sharpley, 1983). Consequently, these slopes are not always characteristic of the adsorbent but depend on various experimental conditions (Sparks, 1986).

Desorption Process

Desorption data plotted according to the first-order kinetic model showed considerable deviation from linearity, with r^2 values ranging from 0.646 to 0.981 (Table 2). This was expected since several mass action rate processes may have been occurring independently. The possibility of multiple first-order reactions corresponding to multiple independent retention sites in the zeolite mineral, similar to the multiple reactions suggested by Griffin and Jurinak (1974) and Jardine and Sparks (1984), was not justified by the data. No distinct breaks in first-order plots were identified. Instead, a gradual change in slope from one time increment to the next was prevalent, indicating a continual change in the apparent rate constant (k_d') and precluding the operation of strictly first-order kinetics.

Table 4. Regression equations and coefficients of determination (r^2) for $\text{NH}_4^+\text{-N}$ desorption using the modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion models, at various pH, initial $\text{NH}_4^+\text{-N}$ concentrations (C_0), and adsorbed $\text{NH}_4^+\text{-N}$ (C^*).

C_0 , mg L ⁻¹	pH	C^* , mg kg ⁻¹ †	Modified Freundlich	r^2	Parabolic diffusion	r^2	Elovich	r^2	Heterogeneous diffusion	r^2
70.1	4	542	$2.459 + 0.092 \log t$	0.997	$339.5 + 9.589t^{1/2}$	0.989	$277.5 + 35.0 \ln t$	0.991	$0.892 + 0.089 \ln t$	0.982
	5	548	$2.458 + 0.095 \log t$	0.996	$338.8 + 9.846t^{1/2}$	0.990	$271.1 + 36.8 \ln t$	0.993	$0.894 + 0.083 \ln t$	0.994
	6	551	$2.472 + 0.090 \log t$	0.995	$343.5 + 9.454t^{1/2}$	0.992	$277.8 + 35.5 \ln t$	0.991	$0.895 + 0.080 \ln t$	0.993
	7	562	$2.501 + 0.086 \log t$	0.996	$364.4 + 9.650t^{1/2}$	0.990	$296.0 + 36.6 \ln t$	0.992	$0.895 + 0.078 \ln t$	0.994
280.2	4	1733	$2.943 + 0.047 \log t$	0.999	$955.4 + 12.58t^{1/2}$	0.964	$874.3 + 45.8 \ln t$	0.996	$0.942 + 0.045 \ln t$	0.998
	5	1751	$2.966 + 0.043 \log t$	0.998	$999.1 + 12.00t^{1/2}$	0.974	$922.6 + 43.4 \ln t$	0.996	$0.946 + 0.040 \ln t$	0.998
	6	1831	$2.974 + 0.042 \log t$	0.998	$1016 + 12.11t^{1/2}$	0.972	$938.6 + 44.0 \ln t$	0.996	$0.946 + 0.040 \ln t$	0.997
	7	1843	$2.988 + 0.042 \log t$	0.999	$1050 + 12.38t^{1/2}$	0.964	$970.5 + 44.8 \ln t$	0.996	$0.948 + 0.044 \ln t$	0.999
560.4	4	2946	$3.264 + 0.028 \log t$	0.987	$1961 + 11.11t^{1/2}$	0.947	$1836 + 52.4 \ln t$	0.981	$0.970 + 0.031 \ln t$	0.963
	5	3018	$3.306 + 0.020 \log t$	0.980	$2122 + 8.82t^{1/2}$	0.906	$2020 + 42.1 \ln t$	0.972	$0.980 + 0.022 \ln t$	0.968
	6	3092	$3.313 + 0.020 \log t$	0.977	$2173 + 7.19t^{1/2}$	0.932	$2108 + 30.5 \ln t$	0.983	$0.978 + 0.021 \ln t$	0.983
	7	3330	$3.320 + 0.020 \log t$	0.990	$2208 + 7.44t^{1/2}$	0.926	$2140 + 31.6 \ln t$	0.980	$0.977 + 0.021 \ln t$	0.991
1401.0	4	5595	$3.557 + 0.017 \log t$	0.995	$3829 + 8.32t^{1/2}$	0.912	$3752 + 35.4 \ln t$	0.973	$0.981 + 0.017 \ln t$	0.997
	5	5728	$3.582 + 0.014 \log t$	0.994	$3978 + 9.00t^{1/2}$	0.937	$3896 + 38.0 \ln t$	0.984	$0.985 + 0.013 \ln t$	0.995
	6	5908	$3.582 + 0.015 \log t$	0.995	$4008 + 8.84t^{1/2}$	0.897	$3926 + 37.8 \ln t$	0.965	$0.984 + 0.015 \ln t$	0.996
	7	5946	$3.592 + 0.012 \log t$	0.995	$4037 + 8.11t^{1/2}$	0.913	$3962 + 34.5 \ln t$	0.973	$0.987 + 0.012 \ln t$	0.997

† C^* is amount of $\text{NH}_4^+\text{-N}$ on the exchange complex of the zeolite before desorption was initiated.

The modified Freundlich model provided a slightly better description of NH_4^+ desorption by the natural zeolite, with r^2 values ranging from 0.977 to 0.999 (Table 4). The parabolic diffusion model provided a satisfactory description of NH_4^+ desorption by the natural zeolite, with r^2 values ranging from 0.897 to 0.992 (Table 4). Conformity to this model suggested that NH_4^+ desorption was a diffusion-controlled process.

The Elovich model had r^2 values ranging from 0.965 to 0.996 and therefore provided a good description of the desorption process (Table 4). Aharoni et al. (1991) and Aharoni and Sparks (1991) have noted that a conformity of experimental data to the Elovich equation indicated by a relatively high r^2 value during an entire experiment could suggest a heterogeneous diffusion process. Aharoni and Sparks (1991) predicted that a

slope <0.24 for the relationship $d(q/q_\infty)$ vs. $\ln t$ would be expected for heterogeneous diffusion. Figures 4 and 5 show plots of q/q_∞ vs. $\ln t$ for adsorption and desorption processes, respectively, that are linear (r^2 values ranged from 0.976 to 0.998 for the adsorption process and 0.963 to 0.999 for the desorption process) across the entire reaction period for all pH and initial NH_4^+ concentrations (Tables 3 and 4). The slopes of these plots ranged from 0.106 to 0.151 for the adsorption process and 0.012 to 0.089 for the desorption process at all pH and initial NH_4^+ concentrations (Tables 3 and 4), suggesting heterogeneous diffusion (Aharoni and Sparks, 1991).

Shell progressive film diffusion and shell progressive particle diffusion models were also evaluated but did not adequately describe NH_4^+ adsorption or desorption by the natural zeolite. The poor fit of these models

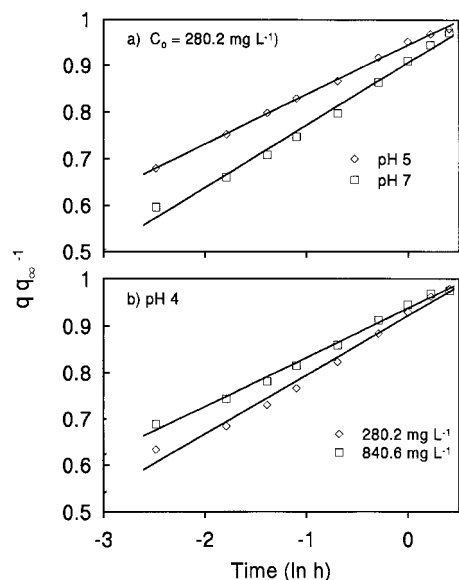


Fig. 4. Ammonium adsorption data applied to a heterogeneous diffusion model at (a) initial $\text{NH}_4^+\text{-N}$ concentration of 280.2 mg L^{-1} at pH 5 and 7, and (b) initial $\text{NH}_4^+\text{-N}$ concentrations of 280.2 and 840.6 mg L^{-1} at pH 4, where q is the amount of $\text{NH}_4^+\text{-N}$ adsorbed by the zeolite at time t and q_∞ is the amount of $\text{NH}_4^+\text{-N}$ adsorbed at 2 h.

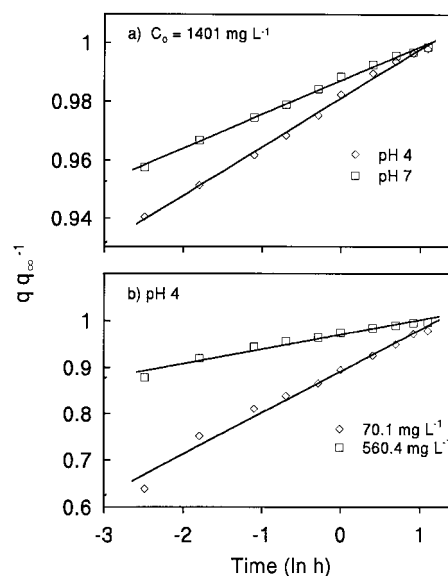


Fig. 5. Ammonium desorption data applied to a heterogeneous diffusion model at (a) initial $\text{NH}_4^+\text{-N}$ concentration of 1401.0 mg L^{-1} at pH 4 and 7, and (b) initial $\text{NH}_4^+\text{-N}$ concentrations of 70.1 and 560.4 mg L^{-1} at pH 4, where q is the amount of $\text{NH}_4^+\text{-N}$ desorbed by the zeolite at time t and q_∞ is the amount of $\text{NH}_4^+\text{-N}$ desorbed at 5 h.

indicated that liquid-filled micropore diffusion and particle film diffusion were not exclusive rate-controlling processes. It is likely that an activated transport process or a combination of several interacting transport processes are rate controlling for the time span observed. Similar observations were made by Allen et al. (1995) while modeling nutrient release in clinoptilolite-phosphate rock systems. We could not find a rigorous solution for the general intermediate case in the literature, in which both particle and film diffusion affect the rate. The mathematical difficulty is that a nonlinear boundary condition at the interface arises (Helfferich, 1983). The problem could probably become simpler if linear concentration profiles in the film are postulated.

Reaction Rate Coefficients

The exchanging groups responsible for the adsorptive capacity of zeolites are known to be dispersed randomly in aqueous solution throughout the pores and capillaries of the zeolite. With NH_4^+ as the exchanging cation, the overall mass transport may be divided into five steps, apart from that effected by the moving liquid: (i) diffusion of NH_4^+ through the solution up to the zeolite particles, (ii) diffusion of NH_4^+ through the zeolite particles, accompanied by the anion in solution (two-dimensional diffusion of the ion along the capillary walls of the zeolite must be considered as a possibility), (iii) chemical exchange between NH_4^+ and exchangeable cations at the exchange site in the interior of the zeolite minerals, (iv) diffusion of the displaced cation out of the interior of the mineral (reverse of step ii), and (v) diffusion of the displaced cation through the solution away from the zeolite mineral (reverse of step i). The kinetics of the exchange will be governed either by a diffusion or by a mass action mechanism, depending on which of the above steps is the slowest.

We calculated the reaction rate coefficients (k) for NH_4^+ adsorption and desorption by the zeolite samples at different pH and initial NH_4^+ concentrations from the modified Freundlich model, and these k values ranged from 0.134 to 0.193 min^{-1} for the adsorption process and 0.129 to 0.226 min^{-1} for the desorption process. Reaction rates are directly proportional to k values (Selim et al., 1976). In this study, measured k values generally decreased with increasing ionic strength, which conforms to Bronsted's activity rate theory (Moore, 1972). Similar observations were made by Doula et al. (1994) on studies of K^+ , which behaves similar to NH_4^+ .

No previous reports on the rate constants for NH_4^+ adsorption or desorption by natural zeolites were found, hence, comparisons with a similar work was not possible. However, our k_a values seemed to be relatively low compared with the k_a values (1–20 min^{-1}) obtained by Sparks et al. (1980) for K^+ sorption in soils. This could possibly be due to slow movement of NH_4^+ ions along the walls of the negatively charged micropores, and to surface diffusion. To clearly visualize this, consider a model based on a system of macropores plus micropores wherein the latter penetrate the walls and feed into the

former. The major portion of the adsorptive capacity will be resident in the micropores. The macropores will merely serve as conduits for the transport of ions to and from the micropores. A practical aspect of these slow NH_4^+ sorption rates is that in situations where zeolites are used as NH_3 or NH_4^+ adsorbents, such as during composting of N-rich wastes or in poultry facilities, high rates of NH_3 emissions could render the zeolite inefficient. Conversely, slowing the rate of NH_3 evolution from the system would allow a prolonged time of contact between NH_3 and the zeolite. Hence, maximum NH_4^+ adsorption can be achieved with time, as a result of slow to moderate diffusion of the NH_4^+ ions into the channels and central cavities of the natural zeolite. One possible way of achieving this high efficiency is by covering the surface of the materials emitting NH_3 with a layer of the zeolite powder. In so doing, the rate of NH_3 escape as it passes through the covering layer of the zeolite will be slowed down, allowing a prolonged period of contact between NH_3 and the zeolite. We have observed this phenomenon in a previous study (unpublished data).

CONCLUSIONS

Initial NH_4^+ concentration and pH were significant factors that influenced the kinetics of NH_4^+ exchange on the natural zeolite. Increasing initial NH_4^+ concentration resulted in decreased NH_4^+ exchange rates. An increase in pH resulted in faster sorption and in greater amounts of NH_4^+ being sorbed. All the tested models provided an adequate description of the NH_4^+ adsorption and desorption processes in the natural zeolite. Conformity of data to the Elovich model and the excellent fit obtained for the heterogeneous diffusion model suggested that the rates of NH_4^+ exchange were governed by a heterogeneous diffusion process. However, the actual mechanism involved can only be determined by experiments designed to evaluate chemical and physical factors affecting the rate constants. The data presented here represent the first use of the first-order kinetic, modified Freundlich, parabolic diffusion, Elovich, and heterogeneous diffusion rate models to describe NH_4^+ adsorption and desorption kinetics in the natural zeolite clinoptilolite at different pH values and initial NH_4^+ concentrations, and indicates that the natural zeolite tested could be used as an NH_4^+ adsorbent and consequently as a controlled-release NH_4^+ fertilizer.

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