

Equilibrium and Kinetic Study of Ammonium Adsorption and Fixation in Sodium-Treated Vermiculite

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ABSTRACT

Ammonium fixation in vermiculite affects the movement of N in many soils. The effects of particle size, solution concentration, pH, and associated anions on NH_4^+ fixation in vermiculite are also important information for reducing N leaching from soils. In this study, the retention of NH_4^+ on the exchangeable and nonexchangeable sites of Montana vermiculite was determined in batch experiments. In the NH_4^+ - K^+ exchange isotherm, the exchangeable sites of the vermiculite exhibited a preference for K^+ to NH_4^+ , while the nonexchangeable sites preferred NH_4^+ to K^+ . The nonexchangeable sites of the sand fraction had a higher preference for NH_4^+ at lower solution NH_4^+ concentration and a lower preference at higher NH_4^+ concentration. An opposite case was observed for the NH_4^+ concentration effect on the preference of nonexchangeable sites in the clay fraction. The retention isotherm of total NH_4^+ in the vermiculite exhibited S-shape curves that can be described by the "two-surface" Langmuir-Freundlich equation. In the kinetic study, the clay fraction adsorbed the largest amount of exchangeable NH_4^+ , but the silt fraction fixed the most NH_4^+ on its nonexchangeable sites. The retention of NH_4^+ in vermiculite increased with solution NH_4^+ concentration. Ammonium adsorption on the exchangeable sites increased at low solution pH, while NH_4^+ fixation was unaffected by pH change. The effect of associated anions was insignificant, except they caused a pH difference in solution.

AMMONIUM PLAYS A KEY ROLE in soil N transformations (Stevenson, 1986, p. 197–215). The contribution of nonexchangeable NH_4^+ release to N availability in soils has been studied extensively since the 1950s (Bower, 1950, 1951; Nommik, 1965; Baethgen and Alley, 1987). Recently, the concerns of possible agricultural N contamination of water resources have generated interest in NH_4^+ retention in soils and clays. Equilibrium and kinetics of NH_4^+ adsorption on exchangeable sites of soil particles have been reported (Dala, 1975; Carski and Sparks, 1987). Similar equilibrium and kinetic characterization of NH_4^+ retention on nonexchangeable sites (often referred to as NH_4^+ fixation) is needed to fully understand NH_4^+ transport in soils. Ammonium fixation in vermiculite affects N transport in many soils (Stevenson, 1986, p. 197–215), yet little is known about the rate of NH_4^+ fixation in vermiculite. Much of the basic information on NH_4^+ fixation originates from studies on K^+ fixation (Nommik and Vahtras, 1982). Further study is needed to verify the assumption that NH_4^+ fixation in soils behaves the same as K^+ because of the similarity of the two ions.

Different models have been applied to describe adsorption and desorption processes. Among them, the discrete surface, the diffuse double layer, and the surface complex models (Sposito, 1984, p. 154–193) dealt with sorption mechanisms. Single-reaction models include both equilibrium and kinetic models. Linear, Langmuir, and Freundlich equations are a few examples of equilibrium models. The kinetic models include zero-order, first-order, second-order, Elovich, and parabolic diffusion equations (Sparks, 1986). Multireaction models usually consist of two or more single-reaction models, for example, the two-surface model (Sposito, 1982) and the two-site or multisite models (Jardine et al., 1985; Amacher et al., 1988). When properly used, models can help the characterization of real reaction processes by reducing a large set of experimental data into a few model parameters.

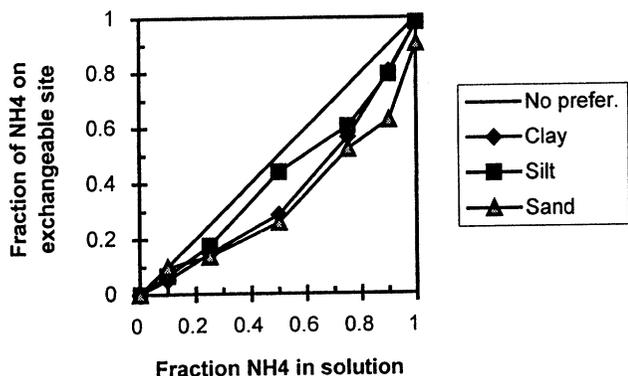
Several factors, besides mineralogical composition, influence the kinetic process of NH_4^+ fixation in soils (Nommik and Vahtras, 1982). Particle size, solution concentration, pH, and associated anions are important factors for NH_4^+ retention in soils. Nommik and others (Nommik, 1965; Nommik and Vahtras, 1982) have documented the effects of these factors on the amount of NH_4^+ fixation, yet little information is available about their effect on the kinetics of NH_4^+ fixation. The purpose of this study was to characterize the equilibrium and kinetic process of NH_4^+ fixation in vermiculite, to compare the reaction characteristics of NH_4^+ retention on exchangeable and nonexchangeable sites of vermiculite, and to investigate the factors that may alter NH_4^+ adsorption and fixation.

MATERIALS AND METHODS

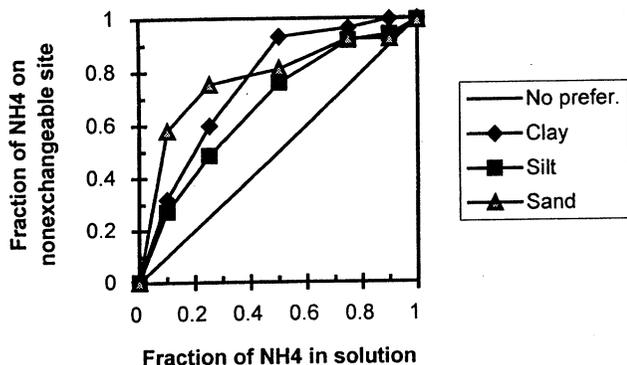
Montana vermiculite (Libby, MT) was obtained from Ward's Natural Science Establishment (Rochester, NY) and used in this study. The mineralogical characterization of Montana vermiculite, which is derived from biotite, was conducted by Alexiades and Jackson (1965) with x-ray diffraction and a chemical (CEC) method. By their CEC method, Alexiades and Jackson (1965) quantitatively determined that clay-size Montana vermiculite contained 62% vermiculite, 28% mica, 9.1% montmorillonite, and 0.5% quartz. Thus, the vermiculite sample used in this study contained mostly (>60%) vermiculite and small quantities of other minerals.

The vermiculite sample was Na-saturated by washing with 1 M NaCl three times, then four times with deionized water (18 M Ω -cm resistivity) to remove excess salts. A portion (10 g) of the sample was separated into clay (<2 μm), silt (2–50 μm), and sand (>50 μm) fractions, using centrifuging and sedimentation methods. These particle-size fractions and a portion of whole vermiculite sample were freeze-dried before being used in the experiments.

a Adsorption Isotherm of Exchangeable NH₄-K in Vermiculite



b Adsorption isotherm of Nonexchangeable NH₄-K



c NH₄-K Isotherm for Both Exchangeable and Nonexchangeable Sites

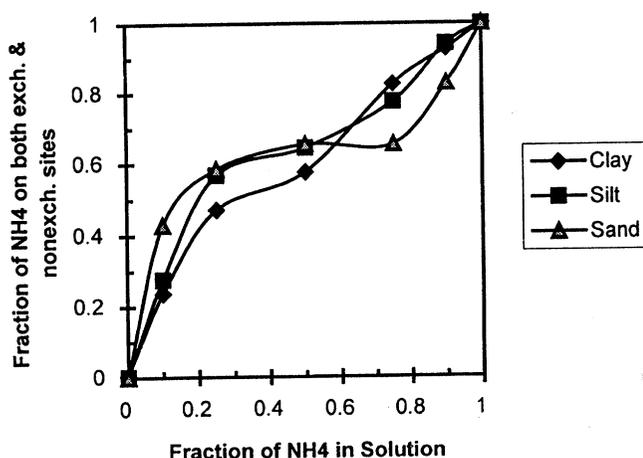


Fig. 1. Retention isotherm of NH₄-K in different particle-size fractions of Montana vermiculite: (a) on exchangeable sites; (b) on nonexchangeable sites; (c) on both exchangeable and nonexchangeable sites.

Exchange Isotherm

The NH₄⁺-K⁺ exchange isotherm was measured by steam distillation and atomic absorption methods. Different particle-size fractions of Na-saturated vermiculite were equilibrated with a series of seven different 1 M Cl⁻ salt solutions containing various molar ratios of NH₄⁺ and K⁺. The molar ratio of NH₄⁺/K⁺ in the solution series was 0:1, 0.1:0.9, 0.25:0.75, 0.5:0.5, 0.75:0.25, 0.9:0.1, 1:0. The equilibration was carried out, in duplicate, by washing and centrifuging 0.1 g of the sample three times with 30 mL of the appropriate exchange solution in a 50-mL polycarbonate centrifuge tube for each treatment. The exchange solution and the sample in the centrifuge tube were allowed to equilibrate at room temperature (22°C) for 0.5 h for the first washing, 2 h for the second, and 24 h for the third on a shaker at a rate of 70 rpm. After the final equilibration with the appropriate exchange solution, the vermiculite samples were washed with deionized water in suspension followed by centrifugation four times before freeze-drying. The freeze-dried samples were reweighed to assure that accurate weights were used in the calculation of the results. Exchangeable NH₄⁺ and K⁺ were extracted by shaking each of the samples (≈0.1 g) with a 25-mL aliquot of 0.5 M CsCl solution in a 50-mL centrifuge tube for 24 h. After the sample was centrifuged, the supernatant was used to determine exchangeable NH₄⁺ and K⁺. The solid residues were digested by 20 mL each of 5 M HF-1 M HCl solution in a polypropylene tube on a shaker for 24 h. The dissolution was used to determine nonexchangeable (fixed) NH₄⁺ and K⁺. The contents of NH₄⁺ and K⁺ were measured by steam distillation (Keeney and Nelson, 1982) and atomic absorption at a wavelength of 766.5 nm (Knudsen et al., 1982), respectively.

Adsorption and Fixation Study

Ammonium adsorption and fixation experiments were carried out using a batch equilibration technique. Adsorption and fixation were initiated by mixing 0.1 g of sample with 20 mL of different NH₄⁺ solutions in 50-mL centrifuge tubes. The tubes were kept at room temperature (22°C) on a shaker at a rate of 70 rpm. Three tubes of each treatment were taken off and centrifuged after reaction times of 0.4, 1, 4, 10, 24, 72, 240, and 720 h. The supernatant was saved for NH₄⁺ measurement. The treated samples were washed three times with deionized water. Exchangeable NH₄⁺ was extracted with 20 mL of 2 M KCl solution. Fixed NH₄⁺ was obtained by digestion in 20 mL of 5 M HF-1 M HCl solution. All NH₄⁺ contents were measured by steam distillation (Keeney and Nelson, 1982). To study the effect of particle size, 0.1 g of clay, silt, or sand fraction was mixed with 20 mL of 0.1 M NH₄⁺Cl + 0.1 M NaCl solution. In the study of other factors, 0.1 g of whole vermiculite sample was mixed with different NH₄⁺ solutions as described below. To investigate the effect of anions, 0.1 M NH₄HCO₃, 0.1 M (NH₄)₂HPO₃, or 0.1 M (NH₄)₂SO₄ solutions were used. In the experiment of varying NH₄⁺ concentration, 0.05 M NH₄Cl + 0.05 M NaCl, 0.01 M NH₄Cl + 0.01 M NaCl, and 0.005 M NH₄Cl + 0.005 M NaCl solutions were used. Various concentrations of NaCl were added to keep the ionic strength relatively constant during the experiments. To study the effect of pH, 0.1 M (NH₄)₂HPO₃/NH₄H₂PO₃ buffer solutions at pH 4.5, 6.0, and 7.5 were used in the experiments.

RESULTS AND DISCUSSION

Adsorption and Fixation Isotherms

In the adsorption isotherm of exchangeable NH₄⁺-K⁺ (Fig. 1a), the vermiculite exhibited a clear preference

Table 1. Calculated model parameters for NH₄-K exchange isotherms in different particle-size fractions of vermiculite using the Freundlich equation.

Sample	<i>r</i> ²	<i>k</i> †	<i>n</i> †
		cmol kg ⁻¹	
Clay	0.992	0.089	1.206
Silt	0.981	0.158	1.011
Sand	0.901	0.054	0.969

† *k* is a reaction coefficient and *n* is an empirical constant.

for K⁺ to NH₄⁺. The differences between the three particle-size fractions were insignificant. The data from the exchange isotherm was used to calculate an NH₄⁺-K⁺ selectivity coefficient (Semmens, 1984), which is similar to an equilibrium constant for the NH₄⁺-K⁺ exchange reaction except that it is expressed in terms of concentration rather than activity:

$$K_{\text{NH}_4\text{-K}} = \frac{\bar{n}_{\text{NH}_4} n_{\text{K}}}{\bar{n}_{\text{K}} n_{\text{NH}_4}} \quad [1]$$

where \bar{n}_{NH_4} and \bar{n}_{K} are the fractions of NH₄⁺ or K⁺ in the vermiculite, and n_{NH_4} and n_{K} are the fractions of NH₄⁺ or K⁺ in the solution. On the average, the NH₄⁺-K⁺ selectivity coefficients for the clay, silt, and sand fractions were determined as 0.46, 0.60, and 0.47, respectively. The coefficients <1.0 imply a preference for K⁺ on the exchangeable sites, while a coefficient of 1.0 means no preference. The nonexchangeable sites preferred NH₄⁺ to K⁺ (Fig. 1b) for all particle-size fractions. The selectivity coefficients were >1.0 for the NH₄⁺-K⁺ fixation isotherm, which indicated a preference for NH₄⁺ on nonexchangeable sites of all particle-size fractions. The sand fraction had a higher preference for NH₄⁺ on nonexchangeable sites than the clay fraction in solutions with lower NH₄⁺ concentration (when solution NH₄⁺/K⁺ ≤ 0.25). The selectivity coefficients were 10.8 and 4.3 for the sand and clay fractions, respectively. The opposite case occurred at higher concentration of solution NH₄⁺ (when NH₄⁺/K⁺ ≥ 0.75), where the clay fraction had a higher preference for NH₄⁺ on nonexchangeable sites than the sand fraction. The respective selectivity coefficients were 17.7 and 2.7 for the clay and sand fractions. The silt fraction of the vermiculite had an average coefficient of NH₄⁺ selectivity ≈ 3.0.

Several equilibrium equations have been used to fit the retention isotherms of exchangeable and fixed NH₄⁺-K⁺. Compared with other equations, the Freundlich equation ($S_e = kC^n$) best described the adsorption

Table 2. Calculated model parameters for NH₄-K fixation isotherms in different particle-size fractions of vermiculite using the Langmuir equation.

Sample	<i>r</i> ²	<i>k</i> †	<i>b</i> †
		cmol L ⁻¹	cmol kg ⁻¹
Clay	0.902	665.7	119.5
Silt	0.920	937.5	126.4
Sand	0.918	923.5	98.0

† *k* is a reaction coefficient and *b* is the maximum retention on the nonexchangeable sites.

isotherm of NH₄⁺ on the exchangeable sites of the vermiculite. In the equation, S_e is the amount of NH₄⁺ on the exchangeable sites (cmol kg⁻¹), *C* is NH₄⁺ concentration in the solution (cmol L⁻¹), *k* is a reaction coefficient, and *n* is a constant. The goodness-of-fit (*r*²) and the model parameters are listed in Table 1.

The Langmuir equation [$C/S_f = 1/kb + (1/b)C$] was among the equations that best described the fixation isotherm of NH₄-K on nonexchangeable sites. The physical meanings of *C* and *k* are the same as described above; S_f is the amount of NH₄⁺ on the nonexchangeable sites (cmol kg⁻¹) and *b* is the maximum retention on the nonexchangeable sites. The reaction coefficient of NH₄⁺ fixation in the clay fraction was smaller than that of the sand fraction, but the clay fraction had a larger maximum of NH₄⁺ fixation than the sand fraction (Table 2). This was consistent with a larger selectivity coefficient for the sand fraction at lower NH₄⁺ concentrations and for the clay fraction at higher NH₄⁺ concentrations.

The retention isotherm of total NH₄⁺-K⁺ in the vermiculite (both exchangeable and nonexchangeable sites) exhibited a similar type of curve (Fig. 1c) to those of a zeolite exchanger with several groups of homogeneous sites (Barrer and Klinowski, 1972). If interference between adsorbed NH₄⁺ on the two types (exchangeable and nonexchangeable) of binding sites can be ignored, we can follow a similar treatment as that of the "two-surface" Langmuir equation (Sposito, 1982) and use a "combined" Freundlich and Langmuir equation:

$$S = \left(\frac{k_f b C}{1 + k_f C} \right) + k_e C^n \quad [2]$$

Figure 1c shows that the Langmuir part of the equation dominated the early stage of the isotherm, while the Freundlich part dominated the late stage after the Langmuir part reached a stable maximum level.

To determine the partition of adsorbed NH₄⁺ between

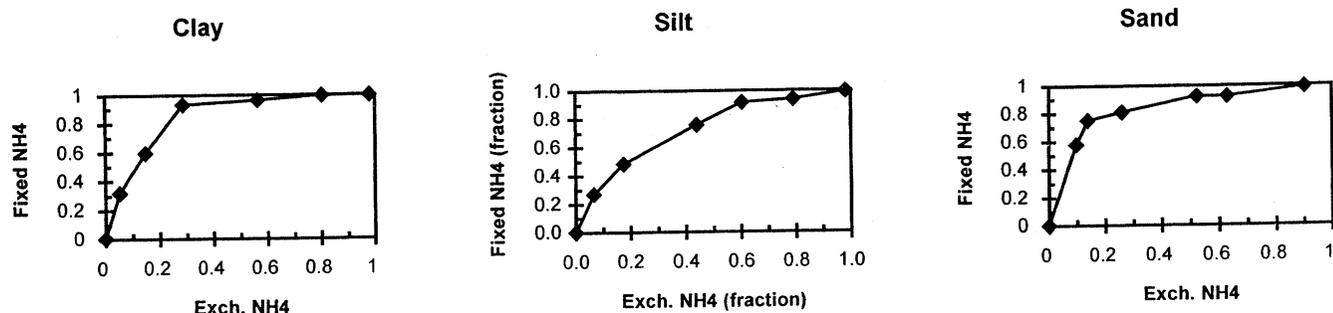


Fig. 2. Partition of adsorbed NH₄⁺ between exchangeable and nonexchangeable sites of Montana vermiculite for different particle-size fractions.

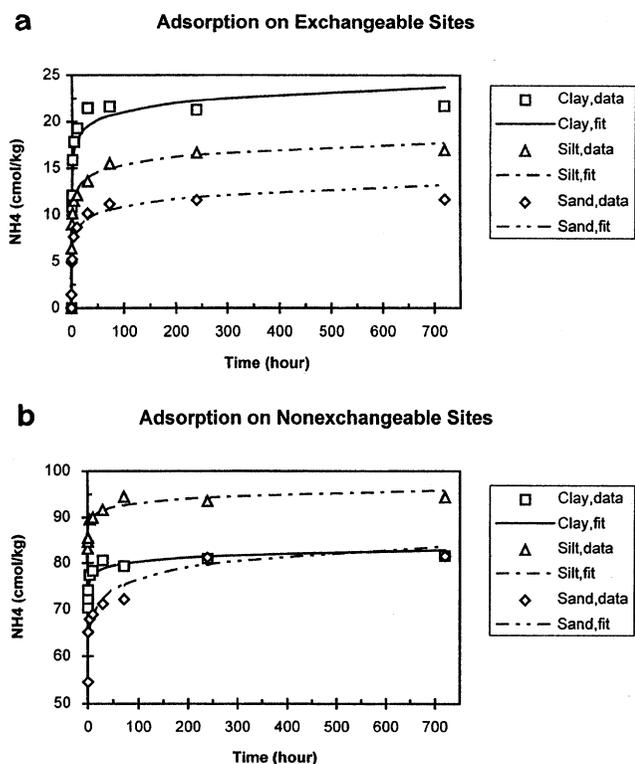


Fig. 3. Kinetic process of NH_4 retention on (a) exchangeable or (b) nonexchangeable sites of Montana vermiculite for different particle-size fractions.

exchangeable and nonexchangeable sites, the amount of fixed NH_4^+ was plotted against the amount of exchangeable NH_4^+ in the vermiculite (Fig. 2). Adsorbed NH_4^+ preferably occupied nonexchangeable sites in the vermiculite first, and took most (60–90%) of exchangeable sites only after 90% of the nonexchangeable sites were occupied (Fig. 2). This phenomenon of preferred partition to nonexchangeable sites for adsorbed NH_4^+ was quite evident for all particle-size fractions, especially the clay and sand fractions.

Kinetic Study of Ammonium Adsorption and Fixation

Among different particle-size fractions of the vermiculite, the silt had a larger amount of exchangeable NH_4^+ than the sand, and the clay had the largest amount of exchangeable NH_4^+ (Fig. 3a, data points). On the

nonexchangeable sites, the sand fraction fixed NH_4^+ as much as the clay fraction, while the silt fraction fixed the largest amount of NH_4^+ (Fig. 3b, data points). The result was consistent with that of Bredell and Coleman (1968), who reported that silt-size particles had a greater ability to adsorb NH_4^+ and retain it against NaCl displacement than clay-size particles. Barshad (1954) showed that a decrease in vermiculite particle size brought about a decrease in NH_4^+ fixation, while others (Nommik, 1965; Nommik and Vahtras, 1982) found that NH_4^+ fixation tended to increase with an increase in the clay content.

Several kinetic models (first-order, Elovich, parabolic, and power-function equations) were used to fit the retention data. The Elovich equation gave the best fit for our experimental results. When applied to ion adsorption in soils, the Elovich equation is generally expressed as (Sparks, 1986)

$$\frac{dS_i}{dt} = \alpha e^{-\beta S_i} \quad [3]$$

Where S_i is the amount of ions adsorbed on type i sites at time t , and α and β are constants. The constant α can be regarded as the initial adsorption rate since $dS_i/dt \rightarrow \alpha$ when $S_i \rightarrow 0$. With the boundary condition $S_i = 0$ at $t = 0$, integration of Eq. [3] gives

$$S_i = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad [4]$$

Simplifying Eq. [4] by assuming $\alpha\beta t \gg 1$ (Chien, 1980a,b), then

$$S_i = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad [5]$$

and letting $a = 1/\beta \ln(\alpha\beta)$ and $b = 1/\beta$,

$$S_i = a + b \ln(t) \quad [6]$$

Since $S_i = a$ at $t = 1$, the parameter a in Eq. [6] represents the amount of NH_4^+ adsorbed or fixed in vermiculite at initial stages. Parameter b reflects the change in adsorption or fixation rates after the initial stage because $\alpha = b \exp(ab)$ and $\beta = 1/b$. The results of regression (Table 3) showed that, for NH_4^+ adsorption on exchangeable sites, the values of a varied with particle size in the order of clay > silt > sand, whereas the values of b were similar for different particle sizes. For

Table 3. Fitting parameters and standard errors (SE) for NH_4 retention in different particle-size fractions of vermiculite using the simple Elovich equation.

Sample	NH_4 type	r^2	b^\dagger	SE	a^\dagger	SE
			$\text{cmol kg}^{-1} \ln(\text{h})^{-1}$		cmol kg^{-1}	
Clay	Exchangeable NH_4	0.878	1.322	0.186	15.0	1.57
	Fixed NH_4	0.925	1.303	0.141	74.3	9.10
	Total NH_4	0.909	2.625	0.314	89.3	2.65
Silt	Exchangeable NH_4	0.982	1.187	0.060	9.8	0.51
	Fixed NH_4	0.939	1.398	0.134	86.5	1.13
	Total NH_4	0.972	2.590	0.165	96.3	1.93
Sand	Exchangeable NH_4	0.932	1.160	0.110	5.5	0.93
	Fixed NH_4	0.921	3.640	0.404	59.6	3.40
	Total NH_4	0.943	4.800	0.446	65.0	3.76

$^\dagger a = 1/\beta \ln(\alpha\beta)$ and $b = 1/\beta$.

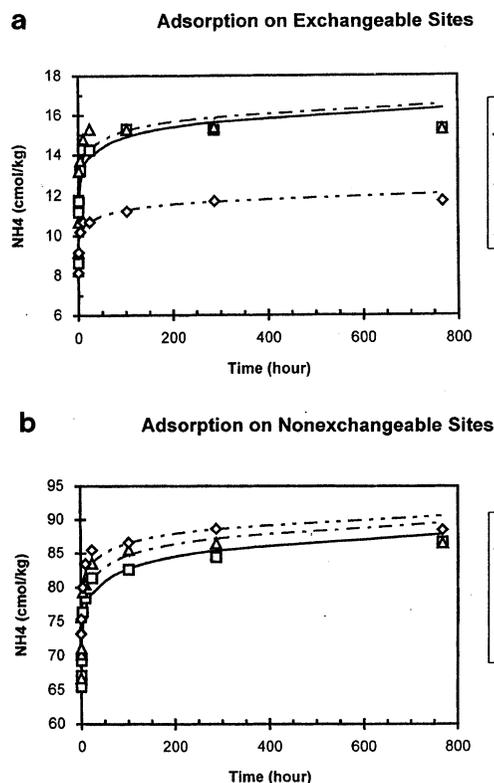


Fig. 4. Kinetic process of NH_4^+ retention on (a) exchangeable or (b) nonexchangeable sites of Montana vermiculite from buffer solutions at different pH.

NH_4^+ retention on nonexchangeable sites, the silt fraction had the highest value of parameter a . The sand fraction had a larger b value, but smaller a value than the clay fraction, which indicates a larger fixation amount of NH_4^+ in the clay than in the sand at the initial stage and a higher fixation rate in the sand fraction than in the clay fraction after the initial stage. This observation is consistent with the results from the equilibrium study and implies a diffusion restriction for NH_4^+ fixation in the sand fraction.

For 0.1 M $(\text{NH}_4)_2\text{HPO}_3$ – $\text{NH}_4\text{H}_2\text{PO}_3$ buffer solutions, lowering solution pH decreased the NH_4^+ concentration in the solution, but NH_4^+ adsorption on the exchangeable sites was greater at solution pH ≤ 6.0 than at 7.5 (Fig. 4a). The effect of solution pH on NH_4^+ fixation in vermiculite was insignificant, as the data set in Fig. 4b shows. The fitting parameters of the Elovich model are listed in Table 4. The values of b and a were similar

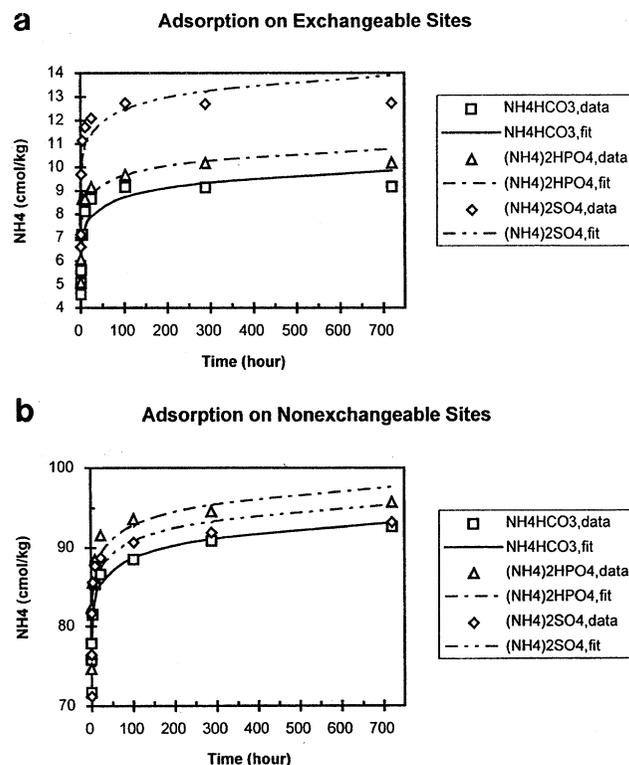


Fig. 5. Kinetic process of NH_4^+ retention on (a) exchangeable or (b) nonexchangeable sites of Montana vermiculite from solutions with different anions.

for NH_4^+ adsorption on exchangeable sites at both pH 4.5 and 6.0. The values of b and a for NH_4^+ adsorption at pH 7.5 were smaller than those at pH 4.5 and 6.0. The difference in the values of b and a was insignificant for NH_4^+ fixation at various pH levels (Table 4). The reason for the increase in NH_4^+ adsorption on the exchangeable sites at lower pH (pH ≤ 6.0) is not understood and needs further study.

The effect of anions (HCO_3^- , HPO_4^{2-} , and SO_4^{2-}) on NH_4^+ fixation in vermiculite was insignificant (Fig. 5b). Both b and a values were similar for NH_4^+ fixation from different solutions (Table 5). However, a difference in NH_4^+ adsorption on exchangeable sites was observed in the solutions of NH_4HCO_3 , $(\text{NH}_4)_2\text{HPO}_4$, and $(\text{NH}_4)_2\text{SO}_4$ (Fig. 5a). The fitting values of the Elovich equation also showed that both b and a values for $(\text{NH}_4)_2\text{SO}_4$ were different from those for NH_4HCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ (Table 5). One possible reason for the difference ob-

Table 4. Fitting parameters and standard errors (SE) for NH_4^+ retention in vermiculite at different pHs using the simple Elovich model.

Solution pH	NH_4^+ type	r^2	b^\dagger	Se	a^\dagger	SE
			$\text{cmol kg}^{-1} \ln(\text{h})^{-1}$		cmol kg^{-1}	
pH 4.5	Exchangeable NH_4^+	0.886	0.712	0.096	11.61	0.83
	Fixed NH_4^+	0.961	2.524	0.192	71.08	1.65
	Total NH_4^+	0.960	3.235	0.251	82.69	2.15
pH 6.0	Exchangeable NH_4^+	0.786	0.658	0.129	12.12	1.12
	Fixed NH_4^+	0.932	2.420	0.250	73.34	2.13
	Total NH_4^+	0.920	3.079	0.343	85.47	2.95
pH 7.5	Exchangeable NH_4^+	0.960	0.401	0.030	9.38	0.27
	Fixed NH_4^+	0.943	2.023	0.188	76.99	1.62
	Total NH_4^+	0.953	2.423	0.203	86.37	1.75

$^\dagger a = 1/\beta \ln(\alpha\beta)$ and $b = 1/\beta$.

Table 5. Fitting parameters and standard errors (SE) for NH₄ retention in vermiculite from solutions with different anions using the simple Elovich equation.

Solution	NH ₄ type	r ²	cmol kg ⁻¹ ln (h) ⁻¹		cmol kg ⁻¹	
			b†	Se	a†	SE
NH ₄ HCO ₃	Exchangeable NH ₄	0.906	0.58	0.070	6.07	0.61
	Fixed NH ₄	0.979	2.30	0.125	78.07	1.10
	Total NH ₄	0.971	2.87	0.188	84.14	1.64
(NH ₄) ₂ HPO ₄	Exchangeable NH ₄	0.924	0.57	0.062	6.99	0.54
	Fixed NH ₄	0.950	2.47	0.220	81.29	1.87
	Total NH ₄	0.949	3.04	0.270	88.29	2.32
(NH ₄) ₂ SO ₄	Exchangeable NH ₄	0.851	0.73	0.115	9.06	0.98
	Fixed NH ₄	0.921	2.26	0.260	79.82	2.23
	Total NH ₄	0.909	3.09	0.369	88.89	3.16

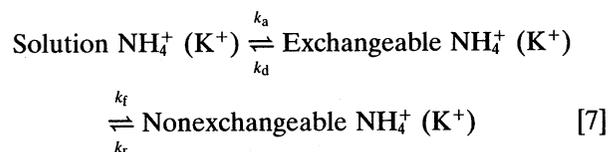
† $a = 1/\beta \ln(\alpha\beta)$ and $b = 1/\beta$.

served may be the effect of the associated anions on the solution pH. The pH values for NH₄HCO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ solutions were 8.26, 7.98, and 5.57, respectively. Consistent with the result in Fig. 4, NH₄⁺ adsorption on exchangeable sites was higher in acid solutions (pH ≤ 6.0) than in basic solutions (pH ≥ 7.5), while NH₄⁺ fixation in vermiculite was unaffected by solution pH.

The adsorption of NH₄⁺ on both exchangeable and nonechangeable sites increased with the NH₄⁺ concentration (Fig. 6). The fitting parameters of the Elovich equation are listed in Table 6. The *a* value for both NH₄⁺ adsorption and fixation increased as the concentration increased from 0.005 to 0.05 M. The *b* value also increased with an increase in NH₄⁺ concentration. The

difference in *b* value between 0.01 and 0.05 M was larger than that between 0.005 and 0.01 M for exchangeable NH₄⁺ (Table 6).

A dynamic equilibrium for different forms of K⁺ in soils and clays has been suggested (Bartholomew and Janssen, 1931; Selim et al., 1976; Sparks and Huang, 1985) and adapted to NH₄⁺ because of the similarity between NH₄⁺ and K⁺ (Nommik, 1965; Nommik and Vahtras, 1982):



where *k_a* and *k_d* are adsorption and desorption rate coefficients, and *k_f* and *k_r* are fixation and release rate coefficients. In this scheme it was assumed that NH₄⁺ (or K⁺) ions adsorbed in clays and soils occupied exchangeable sites first with a fast reaction rate, and then exchangeable NH₄⁺ (or K⁺) slowly transformed to nonexchangeable NH₄⁺ (or K⁺). In other words, NH₄⁺ (or K⁺) would occupy most of the exchangeable sites before they were fixed on nonexchangeable sites because the slow reaction is the rate-determining process. This assumption may be true for K⁺ adsorption and fixation in soils. But our results indicated that NH₄⁺ adsorption and fixation in vermiculite behaved differently. The partition between exchangeable and nonexchangeable sites showed that NH₄⁺ preferably occupied nonexchangeable sites in the vermiculite when only a small portion of the exchangeable sites were occupied by NH₄⁺ (Fig. 2). The NH₄⁺ fixation in vermiculite was as fast a reaction as NH₄⁺ adsorption during the initial stage (Fig. 3–6, data sets). The retention isotherm of total NH₄⁺–K⁺ in vermiculite showed a similar type of curve to those of multisite exchangers (Fig. 1c). All these results support that, for NH₄⁺ retention, the vermiculite behaved as a multisite exchanger (Barrer and Klinowski, 1972; 1973) with at least two types of binding sites (exchangeable and nonexchangeable), on which NH₄⁺ can be adsorbed simultaneously and directly from the solution with different reaction constants. The good fitting of separate Elovich equations to NH₄⁺ exchange and fixation reactions (Tables 3–6) validated the assumption that these two reactions occurred simultaneously between the same liquid phase (the solution) and different solid

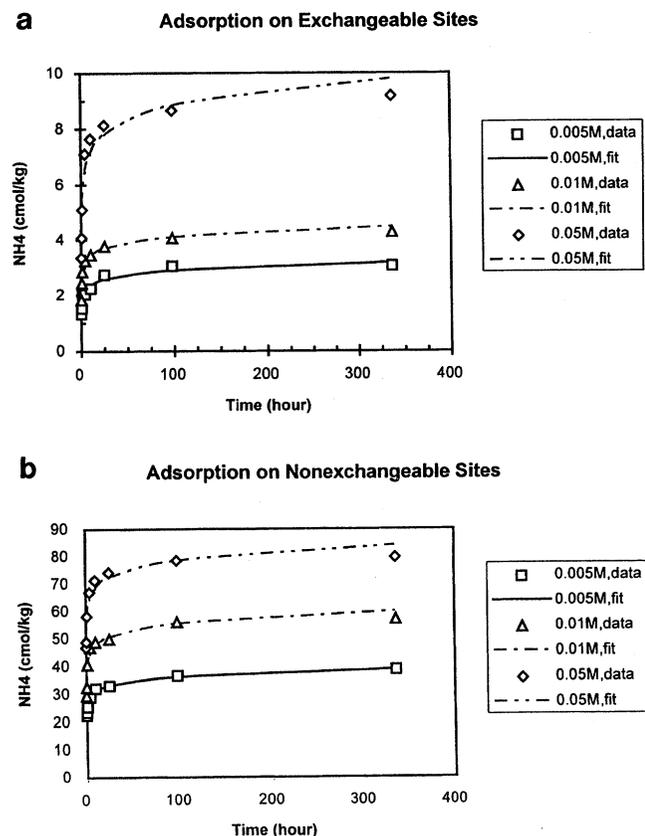


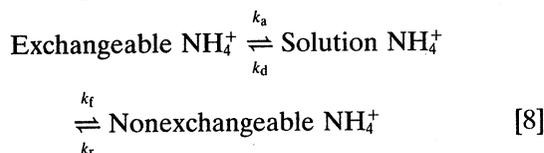
Fig. 6. Kinetic process of NH₄ retention on (a) exchangeable or (b) nonexchangeable sites of Montana vermiculite from solutions at different concentrations.

Table 6. Fitting parameters and standard errors (SE) for NH₄ retention in vermiculite at different solution concentrations and ion strengths using the simple Elovich model.

Concentration	NH ₄ type	r ²	b†	Se	a†	SE
			cmol kg ⁻¹ ln(h) ⁻¹		cmol kg ⁻¹	
0.05	Exchangeable NH ₄	0.950	0.77	0.07	5.29	0.53
	Fixed NH ₄	0.944	4.51	0.45	57.55	3.29
	Total NH ₄	0.946	5.28	0.52	62.84	3.78
0.01	Exchangeable NH ₄	0.977	0.29	0.02	2.72	0.14
	Fixed NH ₄	0.955	3.57	0.32	38.83	2.33
	Total NH ₄	0.958	3.86	0.33	41.55	2.42
0.005	Exchangeable NH ₄	0.949	0.23	0.02	1.84	0.16
	Fixed NH ₄	0.985	2.17	0.11	26.26	0.80
	Total NH ₄	0.988	2.40	0.11	28.01	0.81

† $a = 1/\beta \ln(\alpha\beta)$ and $b = 1/\beta$.

phases (binding sites):



If we use the a and b values in the Elovich equation as rough measures of reaction rates at the initial and later reaction stages, respectively, the results indicated that the values of parameter a were greater for NH₄⁺ fixation than those for NH₄⁺ adsorption (Tables 3–6), which indicated fast NH₄⁺ fixation in vermiculite at the initial reaction stage. The b value for NH₄⁺ adsorption on nonexchangeable sites was similar to or greater than those on exchangeable sites, showing that NH₄⁺ fixation was at least as fast as NH₄⁺ adsorption in vermiculite at the later reaction stage.

CONCLUSIONS

For NH₄⁺ retention, the vermiculite acted as a multi-site exchanger with at least two types of binding sites (exchangeable and nonexchangeable), on which NH₄⁺ can be adsorbed simultaneously and directly from the solution with different reaction constants. All three particle-size fractions of Montana vermiculite exhibited a preference for K to NH₄⁺ on their exchangeable sites in the NH₄⁺-K⁺ exchange isotherm. The fixation isotherm indicated that nonexchangeable sites preferred more NH₄⁺ than K⁺. The sand fraction had a higher preference for NH₄⁺ on nonexchangeable sites than the clay fraction in solutions with lower NH₄⁺ concentration, while the clay fraction had a higher preference for NH₄⁺ on nonexchangeable sites than the sand fraction at higher NH₄⁺ concentration. The retention isotherm of total NH₄⁺ on both exchangeable and nonexchangeable sites exhibited an S-shaped curve, which can be described by the "two-surface" Langmuir-Freundlich equation. Among fractions with different particle size, the clay had the largest content of exchangeable NH₄⁺, but the silt fraction fixed the most NH₄⁺ on its nonexchangeable sites. The retention of total NH₄⁺ in vermiculite increased with solution NH₄⁺ concentration. Ammonium adsorption on the exchangeable sites was larger in acid solutions (pH ≤ 6.0) than in basic solutions (pH ≥ 7.5), while NH₄⁺ fixation in vermiculite was unaffected by solution pH. The effect of associated anions on NH₄⁺ adsorption and fixation

was insignificant, except for their effect on solution pH. Ammonium fixation in vermiculite was a fast reaction occurring at a similar rate to the NH₄⁺ exchange reaction on surface sites.

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