Thermodynamic study for the (NH_4^+ − K^+) exchange on K-saturated clinoptilolite

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Abstract

Homoionic K-clinoptilolite was evaluated as both sink for NH_4^+ and as a source of nutrient such as K^+ through a thermodynamic model. In this model, the isotherm for the exchange reaction, $K_z + (NH_4^+)_s \rightleftharpoons (NH_4)_z + K_s^+$ for different size fraction of clinoptilolite (20–50 and 50–75 μm) was obtained at various charge fractions of $NH_4^+ + K^+$ solution but at total variable concentration of 0.01, 0.1 and 1.0 M. From the thermodynamic data obtained, the mass action quotient (K_m) values, corrected with activity coefficient (K_c) were calculated. These data were plotted as log K_c vs. the equivalent fraction of $(NH_4)_z$ in zeolite to derive the thermodynamic equilibrium constants (K_a). The standard Gibbs free energy ΔG^0 was calculated. From the obtained K_a and ΔG^0 values, it was found that the exchange reaction was favoured at lower concentration (0.01 M) and for small particle size fraction (20–50 μm) of clinoptilolite. The maximum selectivity coefficient (α) values of clinoptilolite (20–50 and 50–75 μm) to NH_4^+ from aqueous solution were found to be 2.4 and 1.9, respectively at lower concentration of 0.01 M.

The effect of anions background on the selectivity of natural clinoptilolite to K^+ and NH_4^+ was studied by calculating the Gapon selectivity coefficient (K_G). The activities of NH_4Cl and KCl used in the exchange solutions were calculated by using Ion Speciation Model (MINTEQ A2/PRODEFA2). The use of CsCl together with the solution mixture of KCl and NH4Cl helps the exchange of NH_4^+ to K^+ due to the role of Cs^+ in displacing K^+ ions. The importance of this study stems from the fact that it throws light on thermodynamics exchange process of NH_4^+ to K^+ and vice versa on the surface of clinoptilolite and consequently between environment containing NH_4^+ and soil amendment containing K^+. © 1997 Elsevier Science B.V.

Keywords: Clinoptilolite; Gapon selectivity; Soil amendments; Thermodynamics of NH_4^+/K^+ exchange

1. Introduction

The utilization of natural zeolites for pollution control depends primarily on their ion exchange capabilities and porous three-dimensional framework structure [1]. Clinoptilolite, $[Ca_x(Na, K)_{6 - 2x}]$, $(Al_6Si_{30}O_{72})\cdot24H_2O$ is one of the most abundant and economically important natural zeolites. Clinop-

tilolite behaviour as an ion-exchange have been the subject of interest for both practical and theoretical reasons [1–10].

The selectivity of clinoptilolite for different inorganic cations determined by Ames [11] has the following order:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+}$$
$$> Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}.$$
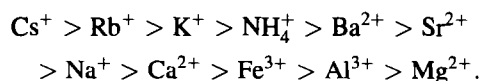
Thus, clinoptilolite is selective for NH_4^+ with respect to all other cations commonly found in

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municipal wastewater except for K^+. As a result, it is the aim of this research to evaluate exchange process using K-saturated clinoptilolite as a soil amendment. This soil amendment serves as both sink for the NH_4^+ and as a source of nutrient such as K^+.

To evaluate the cation exchange ($NH_4^+ - K^+$) system, preliminary thermodynamic data has to be obtained. Furthermore, thermodynamic data are quite useful in the interpretation and understanding of zeolitic exchange equilibria between these cations. The thermodynamic behaviour of the ammonium exchange and the quantities of ammonium removed are very much dependent on the origin of the zeolites, the impurities it contained, as well as its pretreatment [4].

The particle size influenced the basic properties of the zeolite minerals consequently cation exchange rate [12]. Therefore, the ultimate goals of this study are: (1) the prediction and description of the ion-exchange equilibria between K-saturated clinoptilolite and isotherm solutions ($NH_4^+ - K^+$) as a function of solution concentrations to obtain the isothermal data for different size fractions, and to derive the related thermodynamic parameters; (2) the calculation of the MH_4^+ loading by different size fractions of K-clinoptilolite; and (3) the study of the anions background effect on the selectivity of natural clinoptilolite to NH_4^+ ions.

2. Experimental

2.1. Materials and methods

Clinoptilolite in this study was collected from Richmond, North Utah, USA. This mineral was formed as an alteration product of volcanic ash on the tuffaceous member of the Salt Lake Formation in Northern Utah.

The physicochemical and mineralogical properties of the samples collected were examined by Nour El-Dien et al. [13] using X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), chemical and elemental analysis, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and infrared and fourier transform infrared spectroscopy (FT–IR). The sample

collected from Richmond was positively identified as clinoptilolite. It was characterized by a higher Si and Al content (4.90) and a prevalence of K^+ over $Na + Ca$ as in most non-weathered sedimentary deposits.

2.1.1. Separation of particle size fraction

Course fragments were removed by sieving the sample through 75 μm sieve. Representative air-dried samples were dispersed by stirring in deionized water for 5 min and fractionated into very fine sand (75–50 μm), coarse silts (50–20 μm), fine and medium silts (20–2 μm) as follows:

2.1.1.1. Separation of very fine sand.
Air dried sample of 100 g was transferred carefully into 1 l beaker with a minimum amount of deionized water. The sample was dispersed with stirring rod, and it was let to stand exactly for 4 s for each centimeter of suspension depth. The supernatant was decanted slowly through a 300 mesh sieve, and the suspension was collected and transferred to another container labeled '< 50 μm.' The sand was collected from the sieve and allowed to dry in air, and freezed in plastic bags.

2.1.1.2. Separation of coarse silt.
The level of suspension (< 50 μm) was exactly measured. The suspension was stirred well and allowed to settle for 3 min for each 5 cm suspension depth. The suspension was decanted carefully into a bottle labeled (< 20 μm). The sediment was redispersed with water and transferred to a 250 ml standard beaker that had been marked with a line at 5 cm above the inside bottom. Deionized water was added to the marked line and the sediment was allowed to settle for 3 min. The suspension was transferred to the stoppered bottle, labeled (< 20 μm).

Water was added to 5 cm mark, the sample was mixed, allowed to settle for the time calculated by the method of Jackson [14] (2 min and 5 s at 25°C), and the suspension was decanted into a labeled bottle (20–50 μm). The coarse silt was dried in air, and freezed in plastic vials.

2.1.1.3. Separation of fine and medium silt.
Suspension containing the < 20 μm was transferred

to 100 ml centrifuge tubes marked with a line 9 cm from the bottom. The suspension was centrifuged for 2.5 min at 500 rpm. The supernatant was decanted into a bottle labeled ($< 2 \, \mu m$).

The fine and medium silt was obtained by adding water to the content of each tube to the mark, dispersed, and centrifuged for the calculated time (2.9 min at 25°C). The sediment was dried in air, and freezed in plastic bags.

2.1.2. Thermodynamics for the exchange processes

This study involved some experiments on different size fractions at various total concentrations (0.01 to 1.0 M) of exchangeable solutions containing various changed fractions of NH_4^+ and K^+ (0.001 to 0.9 M $NH_4^+ + 0.009$ to 0.1 M K^+). This study was done in order to get the correct thermodynamics of $NH_4^+ - K^+$ exchange process on clinoptilolite.

2.1.2.1. Preparation of homoionic K-clinoptilolite.
Homoionic K-clinoptilolite was prepared by reacting 50 g of clinoptilolite (20–50 and 50–75 μm) with 1 l of 3 M KCl solution using approximately 20 ml exchange solution/g of zeolite at 60°C for two weeks. Full exchange of the K^+ cation involved three steps of mechanical stirring, the sample with 1 l of exchanging solution (KCl). Each step took approximately 5 days including intermediate washing with distilled water till there was no detection of Cl^-. The KCl excess salt of the exchange solution was found to persist with zeolite-requiring therefore many repeated washings were done by ethanol and subsequent ICP analysis up to no detection of K^+ in these washings. The percentage of cation exchange was determined applying the Eq. (1).

$$\% K \text{ Saturation} = \frac{\text{meq of } K^+ / 100 \text{ g Zeolite}}{\text{CEC}} \times 100 \tag{1}$$

where, CEC was the clinoptilolite exchange capacity.

2.1.2.2. Isotherm experiments.
The isotherm experiments at 25°C ± 0.1 were carried out by mixing 0.2 g of K-clinoptilolite (20–50 or 50–75 μm) with 30 ml of $NH_4^+ - K^+$ mixed chloride solutions in stoppered centrifuge tubes. The exchange solutions had varying charge fractions of

NH_4^+ and K^+ (0.01 to 1.0 M), but at constant total concentrations of 0.01, 0.1 and 0.1 M Cl^- salt solutions.

The samples of each fraction were equilibrated with a series of 30 different concentrations in a vibrating water bath at 25°C for one week. To these 30 different concentrations, the summation of NH_4^+ and K^+ concentrations of the first ten fractions was 0.01 M (0.001 to 0.009 $NH_4^+ + 0.009$ to 0.001 K^+), for the second ten fractions it was 0.1 M (0.01 to 0.09 $NH_4^+ + 0.09$ to 0.01 K^+), and for the third ten fractions it was 1.0 M (0.1 to 0.9 $NH_4^+ + 0.9$ to 0.1 K^+) Cl^- total concentrations. After equilibration, the samples were centrifuged and the supernatant was decanted, and the concentrations of both cations in the exchange solutions were measured by recommended procedures. Each treatment was replicated twice.

Ammonium concentration was determined in the exchange solutions and in all subsequent equilibrium experiments using an indophenol–blue colorimetric method [15]. Potassium was measured in this and subsequent experiments using inductively coupled plasma atomic emission spectroscopy (ICP–AES) at wavelength of 766.5 nm. The amount of the adsorbed ammonium was calculated by the difference between the initial and final solution concentrations.

The isotherm curves were obtained by plotting the equivalent fraction of NH_4^+ ion in the solid and liquid phases at equilibrium. The equivalent fraction of NH_4^+ in the solution and on the zeolite was defined as the number of equivalents of NH_4^+ in the particular phase divided by the summation of the equivalents of both ($NH_4^+ + K^+$) ions in that phase as follows:

$$E_{(NH_4)_z} = \frac{N_{NH_4}}{N_{NH_4} + N_k} \tag{2}$$

$$E_{(NH_4)_s} = \frac{m_{NH_4}}{m_{NH_4} + m_k} \tag{3}$$

where, N was the mole fraction of NH_4^+ in the zeolite phase and m referred to the molality in the aqueous phase. The subscript z and s represented the zeolite and solution phases, respectively.

2.1.2.3. Calculation of thermodynamic parameters.
The thermodynamic parameters mass action (K_m), Kielland (K_c) and thermodynamic equilibrium (K_a)

quotients of NH_4^+ adsorption on K-saturated clinoptilolite were calculated based on ion exchange theories [2,10,17–20].

3. Gapon selectivity coefficients (K_G) for NH_4^+ and K^+ on natural clinoptilolite

There are several factors affecting the exchange process between NH_4^+ and K^+ originally present on the clinoptilolite. These are the effect of anions, like Cl^- and CO_3^{2-} and pH values. Therefore, the best method used to calculate the selectivity coefficients of these cations (NH_4^+ and K^+) by clinoptilolite in the presence of these anions is the Gapon method [21].

The ammonium concentrations in the equilibrated solutions were ranged from 0.01 to 0.09 M, and the corresponding concentration ratios, $[NH_4^+]/[K]$ were ranged from 0.1 to 0.9 M/l. After equilibration for 24 h, the solutions were centrifuged and K^+ determined by atomic emission spectrophotometry at $\lambda = 766.5$ nm. The Cl^- concentrations in the equilibrated solutions were analyzed volumetrically using 0.1 N AgNO$_3$ as a titrant. The pH values of the filtrate were measured using an Orion Research Model 701A Digital Ion Analyzer. The single-ion activities of cations in the equilibrated solutions were calculated using the Ion Speciation Model (MINTEQ A2/PRO-DEF A2) [22]. The NH_4^+/K^+ activity ratio in the equilibrated solution and the NH_4^+ fraction solution were calculated.

Determination of the adsorbed NH_4^+ on the clinoptilolite was carried out by extracting 0.2 g samples from equilibrated clinoptilolite solutions four times after 5 min contact with 5 ml of 1.0 M CsCl solution. The supernatant solutions were decanted each time and kept for NH_4^+ and K^+ measurement as previously mentioned.

In this section, the NH_4^+ was measured by phenolate method [23] using Lachat Quikchem Flow Injection Analyzer (LQFIA). This technique was applied in this study in case of using natural clinoptilolite because if K-saturated clinoptilolite is used, a background of KCl reagent can interfered determination of NH_4^+ due to the high amount of K^+ in the zeolite channel which may affect the accuracy of the results.

4. Results and discussions

4.1. Thermodynamic model for $NH_4^+ - K^+$ exchange in K-saturated clinoptilolite

In this study, the isothermal data are used to evaluate thermodynamic model to describe and predict ion-exchange equilibria between different size fractions of K-saturated clinoptilolite and aqueous NH_4^+/K^+ solutions as a function of solution compositions. This study includes the following steps:

4.1.1. Homoionic K-clinoptilolite

Natural zeolite contains a mixture of cations in the framework as exchangeable cations and as impurities complicate any attempt to associate structural/adsorption characteristics of sorbent [3]. Therefore, it is desirable that the cationic form of the ion exchanger is homoionic by different techniques [24–26]. In this study, fully exchanged clinoptilolite sorbents as first time, is successfully achieved by its saturation with K^+ ions as previously explained in the experimental section, and the percentage of K-saturation is calculated by using Eq. (1) and is found to be 100%. Consequently it attains a homoionic form.

4.1.2. Exchange isotherm

The isotherms for the exchange of cations on zeolites are generally classified into five types [12] as shown in Fig. 1.

In this study, two different sizes are used to study the effect of particle size upon the extent of NH_4^+ uptake by K-saturated clinoptilolite. The isotherms of 20–50 and 50–75 μm K-clinoptilolite at 25°C for the $NH_4^+ - K^+$ system at various total concentrations of 0.01, 0.1 and 1.0 M are shown in Fig. 2(a) and (b), respectively. Fig. 2(A, a) refers to the reversible exchange between K^+ and NH_4^+ under the total concentration of 0.01 M of both cations. The first part of the curve refers to the preference of K^+ on clinoptilolite followed by gradual increase of the equivalent concentration $(E-NH_4)_z$ up to the $(E-NH_4)_s = 0.22$. At this equivalent fraction there is arbitrary increase of NH_4 on zeolite. This means that, under this total molarity (0.01 M) a pronounced adsorption of NH_4^+ on zeolite occurs. The use of 0.1 M total concentration
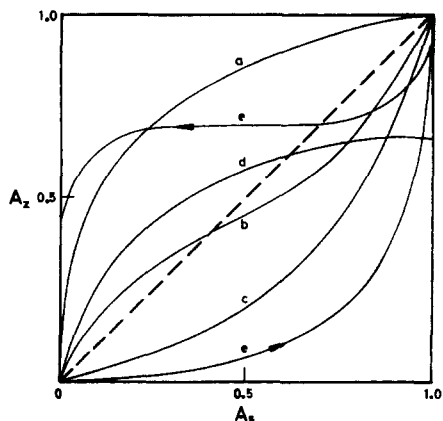
Fig. 1. Types of ion exchange isotherms for the reaction $A_s^+ + B_z$ = $A_z + B_s^+$ are: (a) Selectivity A^+ over the entire range of zeolite composition (L-curve). (b) The A^+ shows selectivity reversal with increasing equivalent in zeolites (S-curve). (c) Selectivity for B^+ over the entire range of zeolite composition. (d) Exchange does not go completion although A^+ is preferred. (e) Hysteresis effects may results from formation of two zeolite phases (h-curve).

E-NH₄ in equilibrating solutions
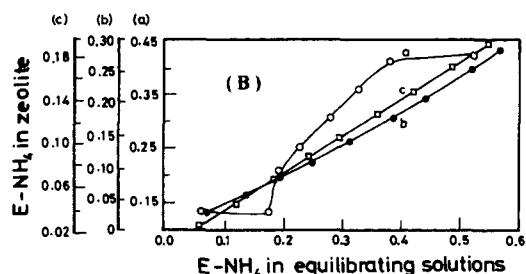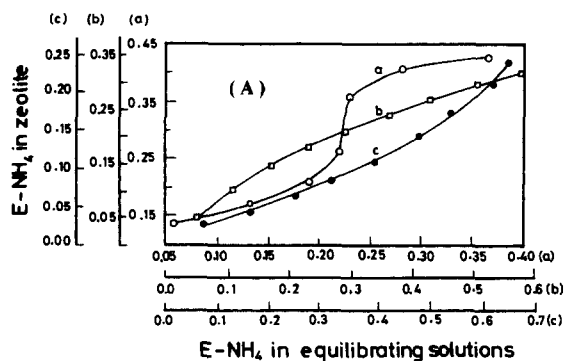

E-NH₄ in equilibrating solutions

Fig. 2. Isotherms of K-clinoptilolite at 25°C and at various total concentrations of $K^+ + NH_4^+$ (a. For 0.01 M; b. For 0.1 M and c. For 1.0 M): (A) In case of 20–50 μm clinoptilolite. (B) In case of 50–70 μm clinoptilolite.

of $NH_4^+ - K^+$ gives an S-curve isotherm (Fig. 2(A) and (b)). This isotherm refers to the preferability of zeolite to adsorb K^+ than NH_4^+ under this condition. Fig. 2(A) and (c) is an L-curve isotherm which shows a high relative affinity of NH_4^+ for the zeolite at this total concentration (1.0 M).

It is concluded that the 20–50 μm K-clinoptilolite adsorb large amount of NH_4^+ ions than K^+ ions at total concentration 0.01 M or 1.0 M, but it is preferable to use 0.01 M at equivalent fraction of NH_4^+ greater than 0.20. These observations are related to the strong hydration of K^+ in dilute solutions which facilitate its releasing as a bulky hydrated ion from zeolite, and consequently the entrance of the less hydrated NH_4^+ instead, on increasing its concentration.

Fig. 2(B (a–c)) show the isotherms of another size fraction of 50–75 μm K-clinoptilolite at 25°C immersed in solutions of $K^+ + NH_4^+$ of total concentrations varied from 0.01 to 1.0 M (ten concentrations in each total molarity). The first isotherm (Fig. 2(B) and (a)) shows no change in the equivalent fraction of NH_4^+ in zeolite up to the equivalent fraction of NH_4^+ in solution of approximately 0.18. After this fraction there is a distinct increase in NH_4^+ adsorption on clinoptilolite as indicated by H-curve isotherm using total molarity of $NH_4^+ + K^+ = 0.01$ M. The other two C-curves isotherms in Fig. 2(B, b) and (B, c) show rare adsorption of NH_4^+ on zeolite as indicated by straight line isotherms.

From these data it is concluded that the adsorption of NH_4^+ on 50–75 μm clinoptilolite occurs at a lower total concentration of $NH_4^+ + K^+$ of 0.01 M, which can be explained in the same way as in case of 20–50 μm as related to the hydration of K^+ in dilute solution.

Fig. 2 illustrates the strong dependence of isotherm shape and clinoptilolite selectivity on total solution concentrations of both $NH_4^+ + K^+$. Generally, the shape of the isotherms is related to the difference in site energies between exchange cations which, in turn, is affected by the cation size differences [27]. The diameter difference of cations under investigation ($NH_4^+ + K^+$) is calculated and found to be 0.3 Å; therefore, they are nearly energetically similar in bonding site toward clinoptilolite. Comparing the above results obtained using two different K-saturated clinoptilolite fractions to adsorb NH_4^+ from $K^+ - NH_4^+$ mixtures, it can be concluded that the

most efficient fraction size for NH_4^+ adsorption in dilute solution is 20–50 μm clinoptilolite.

4.1.3. Explanation of thermodynamic calculation

In order to evaluate quantitatively the changes in position and shape of the above $NH_4^+ + K^+$ isotherms as function of total concentration of external aqueous electrolyte and different particle sizes of the mineral under investigation, it is better to calculate some thermodynamic parameters. These parameters are calculated for different size fractions in terms of the effect of the concentration of external solution upon the K_m, the corrected selectively coefficient (K_c), the thermodynamic equilibrium constant (K_a), and finally on the Gibbs free energy (ΔG^0).

The mass action quotient (K_m) constant is expressed directly in factors of the activities of products and reactants of NH_4^+ and K^+ as follows:

$$K_m = \frac{(E_{NH_4^+})_z (E_{K^+})_s}{(E_{NH_4^+})_s (E_{K^+})_z} \tag{4}$$

The calculations of the K_m constant for the $NH_4^+ - K^+$ exchange process at different total concentrations of 0.01 to 1.0 M for different size fractions are represented in Tables 1 and 2. This constant express the relative preference of the zeolite for competing ion (NH_4^+) over resident ion (K^+).

Correction for the activities of the cation in solution leads to the corrected mass action quotient (K_c) as calculated by,

Table 1

The corrected mass action quotient (selectivity coefficient, K_c), for 20–50 μm clinoptilolite at 25°C calculated from equilibrium constant (K_m) and ammonium equilibrium fractions $(NH_4^+)_s$ and $(NH_4)_z$

$(NH_4)_s$	$(NH_4)_z$	K_m	f_{K/NH_4}	K_c	$\log K_c$
(a) At total concentration of $NH_4^+ + K^+ = 0.01$ M					
0.00025	0.0006	2.4008	0.451	1.084	0.035
0.00057	0.0013	2.2824	0.476	1.087	0.036
0.0013	0.0017	1.3082	0.538	0.704	−0.152
0.0017	0.0023	1.3537	0.575	0.779	−0.108
0.0022	0.0026	1.1823	0.625	0.739	−0.131
0.0028	0.0036	1.5810	0.634	1.002	0.001
0.00281	0.0041	1.4609	0.693	1.012	0.005
0.0041	0.0048	1.1716	0.860	1.007	0.003
(b) At total concentration of $NH_4^+ + K^+ = 0.1$ M					
0.0058	0.0038	0.6539	1.058	0.692	−0.159
0.0135	0.0063	0.4633	1.048	0.485	−0.314
0.021	0.0094	0.4424	1.038	0.459	−0.338
0.027	0.012	0.4377	1.029	0.451	−0.346
0.033	0.015	0.4462	1.022	0.456	−0.341
0.041	0.020	0.4774	1.011	0.483	−0.316
0.046	0.025	0.5318	1.005	0.534	−0.272
0.053	0.030	0.5526	0.996	0.550	−0.259
0.055	0.034	0.6047	0.994	0.601	−0.221
(c) At total concentration of $NH_4^+ + K^+ = 1.0$ M					
0.057	0.037	0.6356	0.346	0.220	−0.658
0.128	0.072	0.5286	0.410	0.217	−0.664
0.202	0.104	0.4585	0.489	0.224	−0.649
0.273	0.130	0.3979	0.580	0.231	−0.636
0.341	0.150	0.3410	0.580	0.233	−0.633
0.501	0.190	0.2329	1.004	0.234	−0.631
0.590	0.208	0.1825	1.241	0.226	−0.645
0.678	0.224	0.1371	1.531	0.210	−0.678

Table 2
The corrected mass action quotient (selectivity coefficient, K_c), for 50–75 μm clinoptilolite at 25°C calculated from equilibrium constant (K_m) and ammonium equilibrium fractions $(NH_4^+)_s$ and $(NH_4)_z$

$(NH_4)_s$	$(NH_4)_z$	K_m	f_{K/NH_4}	K_c	$\log K_c$
(a) At total concentration of $NH_4^+ + K^+ = 0.01$ M					
0.0003	0.0006	2.001	0.417	0.834	−0.078
0.006	0.0013	2.218	0.441	0.979	−0.010
0.0017	0.0013	0.764	0.541	0.414	−0.383
0.0019	0.0021	1.106	0.562	0.621	−0.207
0.0023	0.0025	1.087	0.605	0.685	−0.182
0.0028	0.0031	1.108	0.664	0.736	−0.133
0.0033	0.0036	1.085	0.729	0.791	−0.102
0.0038	0.0041	1.079	0.800	0.863	−0.063
(b) At total concentration of $NH_4^+ + K^+ = 0.1$ M					
0.0071	0.0025	0.349	0.824	0.423	−0.373
0.0015	0.0052	0.343	0.853	0.402	−0.395
0.022	0.0082	0.368	0.881	0.417	−0.379
0.0278	0.011	0.389	0.904	0.430	−0.366
0.0348	0.013	0.365	0.933	0.391	−0.407
0.043	0.0176	0.399	0.969	0.411	−0.385
0.049	0.021	0.416	0.995	0.418	−0.378
0.058	0.025	0.416	1.037	0.401	−0.396
0.060	0.028	0.451	1.046	0.431	−0.365
(c) At total concentration of $NH_4^+ + K^+ = 1.0$ M					
0.069	0.022	0.304	2.019	0.150	−0.823
0.155	0.044	0.251	1.755	0.143	−0.844
0.236	0.067	0.233	1.538	0.151	−0.821
0.313	0.078	0.209	1.356	0.154	−0.812
0.381	0.106	0.193	1.214	0.158	−0.799
0.463	0.127	0.169	1.062	0.159	−0.799
0.5418	0.148	0.147	0.934	0.157	−0.803
0.622	0.171	0.125	0.820	0.153	−0.810

$$K_c = K_m \frac{f_{KCL}}{f_{NH_4Cl}} \qquad (5)$$

The data in Table 1 refer to the decrease of the corrected selectivity coefficient (K_c) as the NH_4^+ fraction in zeolite increases. This trend is noted at all tested concentrations, however the values of the K_c at 0.01 N approximately is double its value in 0.1 M, the K_c in case of 1.0 M is about 1/5 the K_c at 0.01 M. These results refer to the preference of NH_4^+ adsorption on zeolite than K^+ occurs at dilute concentration (0.01 M).

In case of 50–75 μm K-clinoptilolite, the K_c values in Table 2 are decreased as the equivalent fractions of NH_4^+ in zeolite increased at all tested concentrations.

The K_c value at 0.01 M is double its value at 0.1 M, and at 0.1 M it is four times greater in case of 1.0 M. The thermodynamic equilibrium constant, K_a is calculated from the equation [2,16],

$$\ln K_a = \int_0^1 \ln K_c d(NH_4)_z \qquad (6)$$

by plotting ln K_c values (Tables 1 and 2) vs. the equivalent fraction of $(NH_4^+)_z$ and the zeolite phase. The integration is performed mathematically within the limits from $(NH_4)_z = 0$ to $(NH_4)_z = 1$.

In this study, K_a values are calculated for 20–50 and 50–75 μm K-clinoptilolite at various total concentrations of $(NH_4^+ + K^+)$ ranged from 0.01 to 1.0 M at

Table 3
Determination of thermodynamic equilibrium constant and Standard Gibbs Free Energy (ΔG^0) for 20–50 μm and 50–75 μm of K-standard clinoptilolite at various total concentrations of ($K^+ + NH_4^+$)

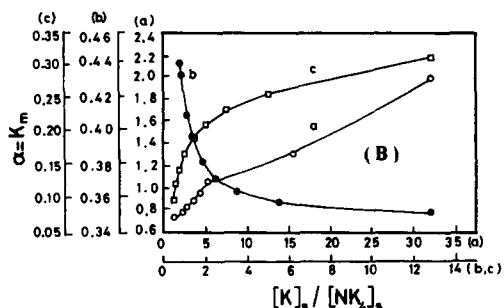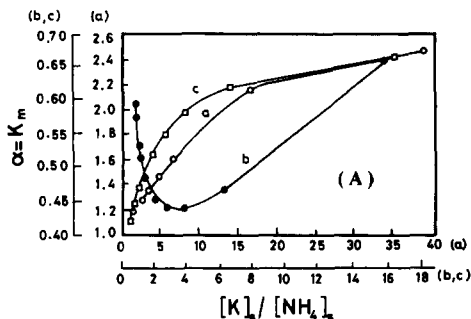| Total concentrations	20–50 μm		50–75 μm	
	K_a	ΔG^0 J mol^{-1}	K_a	ΔG^{0c} J mol^{-1}
0.01 M	12.56	–6269	2.58	–2348
0.1 M	1.40	–833	0.72	813
1.0 M	0.27	–699	0.19	4115

Fig. 3. Ammonium ion loading at 25°C for: (A) 20–50 μm an (B) 50–75 μm K-clinoptilolite at different total concentrations of K^+ and NH_4^+ ions (a. 0.01 M, b. 0.01 M and c. 1.0 M).

25°C (Table 3). For the clinoptilolite under investigation, K_a in small fraction size (20–50 μm) is greater than that in large fraction (50–75 μm). This may be due to the more Si/Al ratio (i.e. high CEC values) in small fraction [13]. It is clear also from Table 3 that the values of K_a are affected by NH_4^+/K^+ ratio and it decreases with the increase in total equilibrium concentration. This behaviour indicates that the exchange reaction between K^+ and NH_4^+ on zeolite is favoured at lower concentrations for small particle size. Therefore, the mathematical thermodynamic calculations of the k_a quantitatively confirms the qualitative conclusion that previously obtained from the isothermal curves which are used in these calculations.

A Gibbs standard free energy, ΔG^0, always calculated for cation exchange reactions by the use of

$$\Delta G^0 = -RT \ln K_a \qquad (7)$$

If ΔG^0 is negative, the exchange reaction is favorable i.e. $K_a > 1$. In this work, the ΔG^0 change to a more positive values with the increase of total concentrations in case of the large size fraction (50–75 μm) where it is negative in case of small size fraction (20–50 μm). The results of ΔG^0 (Table 3) indicate that there is a more pronounced exchange of K^+ with NH_4^+ in case of small size fraction of clinoptilolite than on using the 50–75 μm fraction, especially in dilute 0.01 M total concentration of ions. This result is also previously achieved from the qualitative study on the isotherms (Fig. 2).

4.2. Ammonium ion loading

A method developed by Ames [11] depending upon the calculation of selectivity coefficient (α) can be

used to estimate clinoptilolite ammonium ion loading from the previously obtained equilibrium data (Fig. 3).

Fig. 3 shows the plot of α vs. $[K]_s/[NH_4^+]_s$ in case of clinoptilolite fraction of 20–50 μm at various $[K^+ + NH_4^+]$ total concentration in solution. Fig. 3(A), curves (a–c), shows α increase with change ratio of K^+/NH_4^+ in solution increase, and the maximum value of α is 2.4 in case of 0.01 M total concentration of both ions, which is more larger than its values at 0.1 M (curve b) and 1.0 M (curve c). Therefore, the ammonium loading is large in case of 0.01 M.

The inspection of the plot of α vs. $[K^+/NH_4^+]$ ratio in case of the size fraction 50–75 μm (Fig. 3B) refers to the maximum value of α is 1.9 at 0.01 M solution (curve a). Fig. 3(b) shows the decrease of α with K^+/NH_4^+ increase. Comparing the values of α with molarity of total concentration of $NH_4^+ + K^+$, it can be ordered that α is of 0.01 M > 1.0 M > 0.1 M. On the other side, α decreases with the increase of the ammonium loading on clinoptilolite at various mola-

rities of (NH_4^+ + K^+) but it is more better in dilute solution of 0.01 M. Generally, in literature it is always found that as the loading of specific cation increases onto a zeolite the selectivity of the zeolite for that cation decreases [11]. This means that as the ammonium loading increases onto a clinoptilolite, its selectivity (α) for NH_4^+ decreases. This also means that varying the charge fraction ratio of K^+/NH_4^+ on the clinoptilolite helps in the detection of the charge fraction ratio of K^+/NH_4^+ in solution.

From these data several relationships can be obtained concerning clinoptilolite equilibrium with NH_4^+ and K^+ solutions. Firstly, it is clear from the comparison of α with K^+/NH_4^+ ratio (usually expressed as K/N) that α always decreases on decreasing this ratio as various total molarities (K^+ + NH_4^+) decreases.

Generally, the consumption of any nutrient by the plant is always at the expense of the other one. This consumption depends mainly on the above ratio. Therefore, as indicated from the above results, if K^+/NH_4^+ charge ratio in solution is large, this means that clinoptilolite NH_4^+ adsorption is large. If K^+/NH_4^+ charge fraction ratio in solution is small it means ammonium loading on mineral is small.

The inspection of the above data also shows that the ammonium loading is easily possible on mineral of small fraction size than that of large fraction, especially in dilute solution. It is strongly recommended that the potassium clinoptilolite should be used as a soil amendment to provide either K^+ or NH_4^+ to the plant or to keep any one of them on its surface, by the variation of fraction and/or K^+/NH_4^+ charge fraction ratio.

4.3. Determination of Gapon selectivity coefficient (Solution-exchange phase interaction)

The selectivity of clinoptilolite to ammonium in homoionic systems is affected by anionic portion of the medium and/or that of the zeolite. The study of this effect can be achieved by the calculation of Gapon selectivity coefficient [21].

For homovalent exchange reactions like that under investigation and contraction of cation when it is equal to activity this method can be applied, and the Gapon coefficient is expected to be a constant and equal to the selectivity [28].

The Gapon selectivity (K_{gex}) for natural clinoptilolite can be expressed for the following equilibrium:

$$NH_4Cl + K^+ - clinoptilolite(NH_4^+)_z + KCl$$
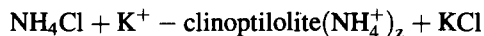
by,

$$K_{Gex} = \frac{a_{NH_4^+} \cdot a_{KCl}}{a_{K^+} \cdot a_{NH_4Cl}} \qquad (7a)$$

The activities of a_{KCl} and a_{NH_4Cl} are calculated by the use of Ion Speciation Model (MINTEQ A2/PRO-DEF A2). The Gapon selectivity coefficient K_G can be obtained from K_{Gex} assuming that zeolite exchange activity (a) is equal to its equivalent reaction [21]. Therefore,

$$K_G = \frac{a_{NH_4^+} \cdot (E_{K^+})_z}{a_{K^+} + (E_{NH_4^+})_z} \qquad (8)$$

where, E is the equivalent fractions of cations in their solution. These fractions are actually calculated as follows:

$$E_{NH_{4+}} = \frac{Ex_{NH_{4+}}}{Ex_{NH_{4+}} + Ex_{K^+}} \qquad (9)$$

where, Ex = exchanged cation (meq/100 g zeolite).

Usually CsCl helps in the removal of K^+ adsorbed by clinoptilolite, because Cs is very efficient in such removal. The activity ratio of NH_4^+ and K^+ cations in the equilibrium solution, the fraction of these exchangeable cations, and the K_G for clinoptilolite (20–50 μm) are presented in Fig. 4.

Fig. 4 shows the values of activity ratio NH_4^+/K^+ in relation to the exchanged fraction of NH_4^+ and the K_G for 20–50 μm clinoptilolite in chloride medium for
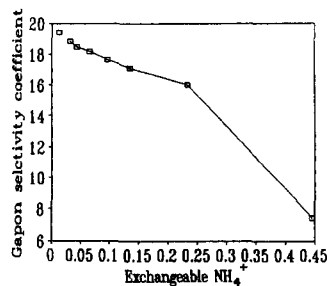

Fig. 4. Gapon selectivity coefficients (K_G) vs. exchanged ammonia on K-clinoptilolite of 20–50 μm size.

nine different concentrations of each K^+ and NH_4^+ components (0.01 to 0.09 M NH_4^+) and of total concentrations constant of 0.1 M.

The inspection of Fig. 4 refers to the regular variation of Gapon K_G with $[NH_4^+]_z$. The decrease in this selectivity refers to the lower ammonium loading on zeolite in a similar way like that in case of α selectivity coefficient (Fig. 3) and the thermodynamic equilibium constant K_a (Table 3).

It is also noticed that ammonium loaded on zeolite is affected by its fraction in adsorption media. Its value increased with the increase of $[NH_4^+]_s$ fraction and the decrease of K^+ fraction up to 0.07 M of K^+. It decreases when the molarity of both the cations are near to each other (0.04 to 0.06, 0.05 to 0.05 and 0.06 to 0.05 K^+ to NH_4^+). This may be related to the high competition between K^+ and NH_4^+ at equal concentrations. The ammonia loaded on zeolite starts to increase again when $[NH_4^+]$ exceeds 0.07 M and consequently Gapon selectivity (K_G) decreases. This variation of K_G with ammonium fraction loaded is shown in Fig. 4. It shows a distinct abrupt decrease of K_G at $[NH_4^+]_z = 0.25$ meq/100 g zeolite. Finally, it is concluded that the behaviour of ammonium loading on clinoptilolite is unaffected by the presence of Cl^- and it agrees that the conclusion comes from calculation of K_a and α.

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