Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite

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Abstract

A study on ion exchange kinetics and equilibrium isotherms of ammonium ion on natural Turkish clinoptilolite (zeolite) was conducted using a batch experiment technique. The effects of relevant parameters, such as temperature, contact time and initial ammonium (NH_4^+) concentration were examined, respectively. The pseudo first-order, pseudo second-order kinetic models and intraparticle diffusion model were used to describe the kinetic data. The pseudo second-order kinetic model provided excellent kinetic data fitting ($R^2 > 0.990$) and intraparticle diffusion effects ammonium uptake. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms for ammonium uptake and the Langmuir model agrees very well with experimental data. Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also determined. An examination of the thermodynamic parameters shows that the exchange of ammonium ion by clinoptilolite is a process occurring spontaneously and physical in nature at ambient conditions ($25\,^\circ C$). The process is also found to be exothermic. The results indicate that there is a significant potential for the natural Turkish clinoptilolite as an adsorbent material for ammonium removal from aqueous solutions.

1. Introduction

The ammonia sources, which are municipal, agricultural and industrial, contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. Complete removal of ammonia from process or waste effluents is required due to its extreme toxicity to most fish species. A variety of biological and physicochemical methods and technologies have been proposed for the removal of ammonia from the environment and industrial water systems [1]. The traditional method for ammonium removal from municipal and industrial wastewaters is based on biological treatments. Since biological methods (nitrification–denitrification) do not respond well to shock loads of ammonia, unacceptable peaks may appear in the effluent ammonium concentration. As discharge limits of various pollutants becomes more stringent, ion exchange and adsorption become more interesting as possible treatment methods. Ion exchange with natural zeolites is more competitive because of its low cost and relative simplicity of application and operation. The use of natural zeolite for the removal of ammonia from water and wastewater appears to have potential due to the advantages and peculiarities over some conventional and expensive ion-exchange resins [2,3].

Natural clinoptilolite (zeolite) has a three-dimensional crystal structure and its typical unit cell formula is given either as $Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$ or $(Na_2, K_2, Ca, Mg)_3 [(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$ [4,5]. Three-dimensional crystal structure of zeolite contains two-dimensional channels [6], which embody some ion exchangeable cations such as Na, K, Ca and Mg. These exchangeable cations give rise to the ion-exchange properties of the material [7,8]. Such sorptive properties have been utilized for a variety of purposes such as adsorption of ammonia by natural clinoptilolite [9–12], removal of metal ions [13–15] and dye contaminants [16–18]. However, little investigation has been conducted to determine the kinetics of ammonium exchange using natural zeolite. The main

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Table 1
Chemical analysis of clinoptilolite

Constituent	Value (wt.%)
SiO_2	74.4
Al_2O_3	11.5
Fe_2O_3	1.1
K_2O	5.0
MgO	0.5
Na_2O	0.6
CaO	2.0
TiO_2	0.1
MnO_2	<0.001
P_2O_5	0.02
Loss of ignition	5.85

Fig. 1. Effect of contact time and initial concentration on the exchange of NH_4^+ onto clinoptilolite (T, 40 °C, solid concentration, 10 g/L; agitation rate, 200 rpm).

objective of this paper is to describe the characteristics of a natural clinoptilolite from Turkey (Esen Foreign Trade Co.), to investigate the kinetics and the equilibrium of ammonium ion removal by clinoptilolite and to determine the factors controlling the rate of process.

2. Material and methods

Sample of clinoptilolite was obtained from the Esen Foreign Trade Co. in Western Anatolia, Turkey. Samples were crushed and classified to a size range of 1.0–1.4 mm. Clinoptilolite was washed to remove the water soluble residues and other undesirable material, and dried in an oven at 100 ± 5 °C for 24 h. Chemical and physical properties of sample was supplied by the producer. Mineralogical content of 85% is clinoptilolite, 10% is feldspar and 5% is clay. Cation exchange capacity and bulk density of are 0.95–1.4 meq/g and 900–1100 kg/m^3, respectively. Chemical properties of the clinoptilolite sample are summarized in Table 1.

The ion exchange of NH_4^+ ion on clinoptilolite was carried out using a batch method. The batch experiments were conducted using 0.5 g of adsorbent with 50 mL of solutions in the range of 25–150 mg/L initial NH_4^+ concentrations. Synthetic ammonia solutions were prepared by dissolving NH_4Cl salt (analytical purity), in distilled water. The bottles were placed on Gallenkamp orbital shaker at 25, 40 and 55 °C and centrifuged at 200 rpm. The equilibrium concentrations of ammonium were determined analyzing samples after centrifugation in the laboratory with the colorimetric method using the Nessler solution. Distilled and deionized water with a conductivity value of 2×10^{-6} mho s/cm was used in all experiments. Ammonium uptake (q_e) was calculated using the following equation:

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

where q_e (mg/g) is the amount of total adsorbed ammonium ions (mg/g), C_0 and C_e are initial and equilibrium concentrations of ammonium in solution (mg/L), respectively. V (L) is the solution volume and M (g) is the adsorbent weight.
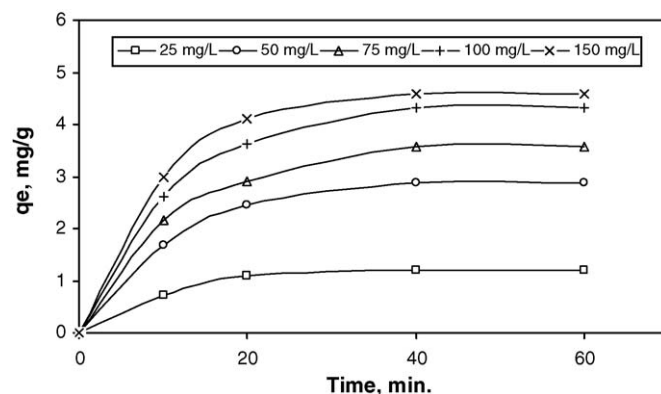
3. Results and discussion

3.1. Equilibrium studies

3.1.1. Effect of initial ammonium concentration

Ammonium exchange by natural clinoptilolite was studied at different initial NH_4^+ concentrations in the range of 25–150 mg/L. As shown in Fig. 1, ammonium exchange capacity increased with increasing of initial NH_4^+ concentration and this is the result of an increase in the driving force. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface [19]. For lower initial concentration of the NH_4^+, equilibrium time was lower than higher concentration because the increased competition for the active sites with increasing in NH_4^+ concentration. This is consistent with the ion-exchange surface becoming increasingly saturated with ammonium ion [12].

3.1.2. Effect of contact time

Fig. 1 shows the ammonium uptake as a function of contact time at 40 °C. The amount of exchanged NH_4^+ increased with an increase in the contact time for any initial concentration and equilibrium was established in 40 min. It was observed that more than 70% of final NH_4^+ uptake was completed within 10 min and then removal rate became slow with the increase of contact time. This is caused by fast diffusion onto the external surface then followed by fast pore diffusion into the intraparticle matrix to attain equilibrium [14,19]. Dimova et al. [20] also found that ammonia uptake by zeolite was a fast process that occurred with less 15 min.

3.1.3. Effect of temperature

The effect of temperature on ammonium exchange was studied at 25, 40 and 55 °C, and the results were shown in Fig. 2. The results indicate that the amount of NH_4^+ exchanged onto clinoptilolite increases with a decrease in temperature, and this may be due to a tendency for the ammonium molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution [21]. Also decreasing of ammonium exchange capacity with increase in the temperature indicates that uptake
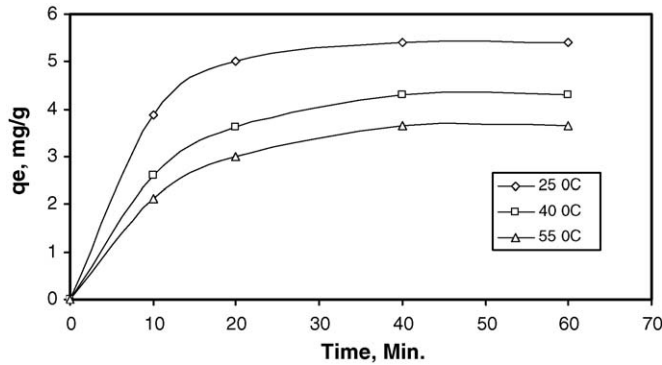
Fig. 2. Effect of temperature on the exchange of NH_4^+ by clinoptilolite.

of NH_4^+ onto clinoptilolite is controlled by an exothermic process [22].

3.2. Ammonium exchange isotherms

The ion exchange isotherms characterize the equilibrium of an ion in solid phase with the concentration of the ion in solution [23]. The exchange of NH_4^+ on the clinoptilolite was analyzed using Langmuir and Freundlich isotherm models. The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the equilibrium amount of NH_4^+ exchanged by clinoptilolite (mg/g), C_e is the equilibrium NH_4^+ concentration in the solution (mg/L), q_{max} (mg/g) is the maximum uptake of ammonia exchanged and K_L is the Langmuir constant (L/mg). q_{max} and K_L constants were calculated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively (Fig. 3).

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L, which was defined by Ho and McKay [24] as:

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where R_L is a dimensionless separation factor, C_0 is initial concentration (mg/L) and K_L is the Langmuir constant (L/mg). The
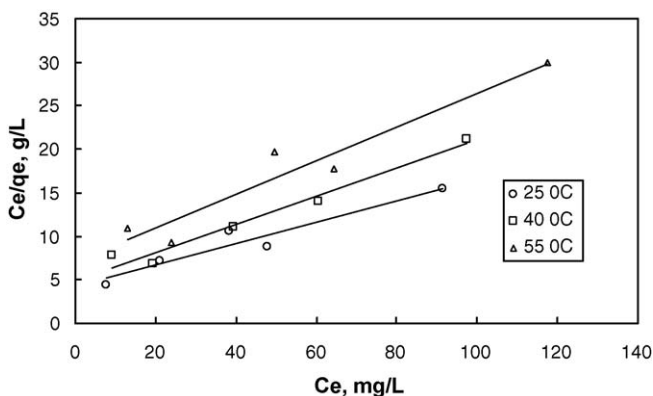

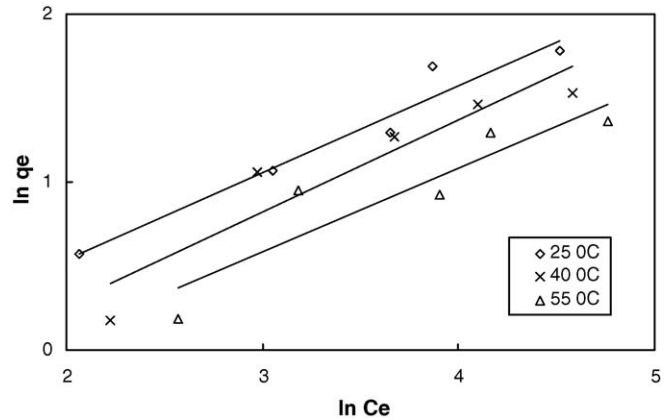Fig. 3. Langmuir plots for the ammonium exchanged.

Fig. 4. Freundlich plots for the ammonium exchange.

calculated values of separation factor are shown graphically in Fig. 5.

The linear form of Freundlich equation is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where K_F is Freundlich constant (L/g) and $1/n$ is the heterogeneity factor. Freundlich constants were calculated from the slope and intercept of Fig. 4 and are given in Table 2.

The isotherm constants and correlation coefficients are given in Table 2. Comparing the correlation coefficients in Table 2 reflects that Langmuir model yield a much better ($R^2 = 0.927$–0.969) fit than that of the Freundlich model ($R^2 = 0.878$–0.952). K_L and K_F constants decreased with increasing temperature and this indicates an exothermic reaction for ammonium exchange by clinoptilolite [25]. Also the magnitude of $1/n$ constant for Freundlich isotherm changes between 0 and 1 and it is a measure of exchange intensity or surface heterogeneity. As seen in Table 2 the values of $1/n$ for all temperatures were smaller than 1 and it represent the favorable removal conditions [26]. Additionally, the R_L values as seen in Fig. 5 were in the range of 0–1 indicating that the exchange of NH_4^+ by clinoptilolite is favorable.

3.3. Kinetics of ammonium exchange

The pseudo first (Lagergren), second-order and diffusion models were used for analysis of exchange kinetics. According to Motoyuki [27], the Lagergren's equation for first-order kinetics can be written as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

Table 2
Isotherm constants for the ammonium exchange by clinoptilolite

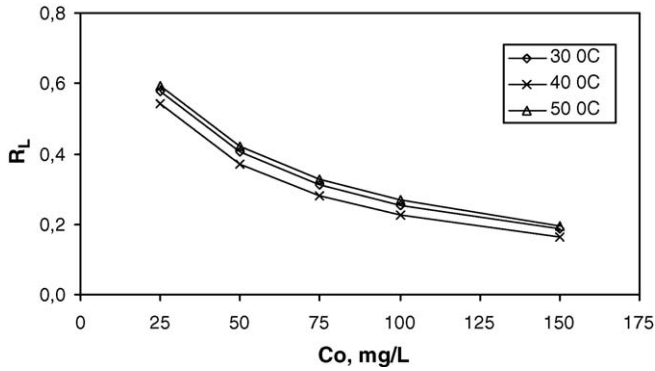| T (°C)	Langmuir constant			Freundlich constant		
	q_{max} (mg/g)	K_L (l/mg)	R^2	$1/n$	K_F (l/mg)	R^2
25	8.121	0.029	0.927	0.517	0.612	0.952
40	6.149	0.034	0.969	0.550	0.437	0.878
55	5.166	0.027	0.927	0.498	0.405	0.929

Fig. 5. Separation factor (R_L) of NH_4^+ exchanged by clinoptilolite (agitation rate, 200 rpm; solid concentration, 10 g/L).

Table 3
Comparison of pseudo first-order, second-order and diffusion models

T (°C)	Pseudo second-order			Pseudo first-order R^2	Diffusion R^2
	q_{e2} (mg/g)	k_2 (g/mg min)	R^2		
25	5.95	0.03	0.998	0.972	0.913
40	4.95	0.026	0.996	0.985	0.857
55	4.42	0.020	0.990	0.962	0.917

where q_e and q_t are the amount of ammonium exchanged (mg/g) at equilibrium and at time t, k_1 is the rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus t should give a linear relationship with the slope of $k_1/2.303$ and intercept of ($\log q_e$).

Pseudo second-order model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{1}{q_{e2}} t \qquad (6)$$

where k_2 is the rate constant (g/mg min). Values of k_2 and q_{e2} were obtained from the straight-line plots of t/q_t against t and are given in Table 3. Pseudo second-order kinetic plotted at different temperatures are given in Fig. 6.

The intraparticle diffusion equation can be written by following:

$$q_t = k_d t^{1/2} + C \qquad (7)$$

where k_d is the intraparticle diffusion rate constant (mg/g^{-1} min$^{-1/2}$) and C is the intercept. Fig. 7 presents plots of q_t versus $t^{1/2}$ for at various temperatures studied.
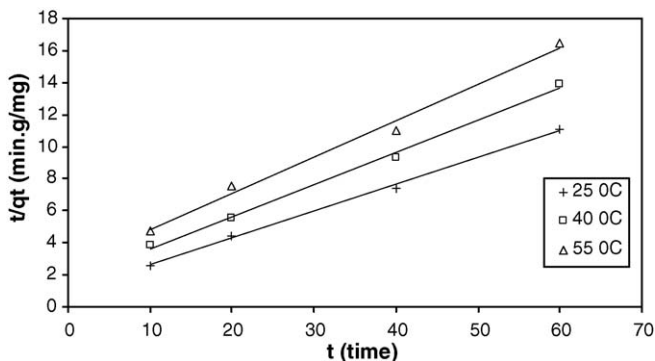

Fig. 6. Pseudo second-order kinetic plots for ammonium exchange by clinoptilolite at different temperatures.
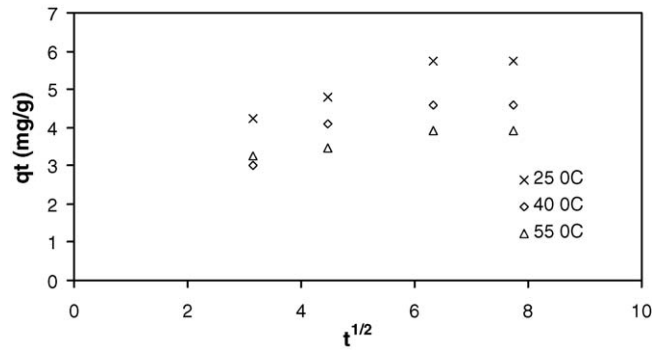

Fig. 7. Intraparticle diffusion kinetic plots at different temperatures.

Table 4
Change of thermodynamic parameters with temperature

Temperature (°C)	K_C	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/K mol)
25	1.09	−0.22	−22.34	−74.42
40	0.66	1.09		
55	0.55	1.60		

Comparing the correlation coefficients in Table 3, the higher coefficient correlation values confirm that the ammonium uptake by clinoptilolite follows pseudo second-order model ($R^2 > 0.990$). The values of pseudo second-order model constant decreases with increasing temperature. As can be seen from Fig. 7, ammonium exchange by clinoptilolite involves two stages. These two stages suggest that the ammonium exchange process proceeds by surface sorption and intraparticle diffusion. The first linear portion is attributed to the boundary layer diffusion effect and the final linear portions may be due to the intraparticle diffusion effect [28,29].

3.4. Thermodynamic parameters

The amount of NH_4^+ exchanged at equilibrium at different temperatures for 25, 40 and 55 °C was examined to obtain thermodynamic parameters. Changes in the standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using following equations:

$$K_C = \frac{C_{Ae}}{C_{Se}} \qquad (8)$$

$$\Delta G^0 = -RT \ln K_C \qquad (9)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (10)$$

where K_C is the equilibrium constant, C_{Ae} is the amount of NH_4^+ uptaked on the clinoptilolite per L of the solution at equilibrium (mg/L), C_{Se} is the equilibrium concentration of the NH_4^+ in the solution (mg/L). T is the solution temperature (K) and R is the gas constant and is equal to 8.31 J/(mol K). Eq. (10) represents a mathematical relationship between K_C and $1/T$. ΔH^0 and ΔS^0 were calculated from the slope and intercept of linear plot of $1/T$ versus K_C (Fig. 8). The values of K_C, ΔG^0, ΔH^0 and ΔS^0 parameters are summarized in Table 4. Change in the
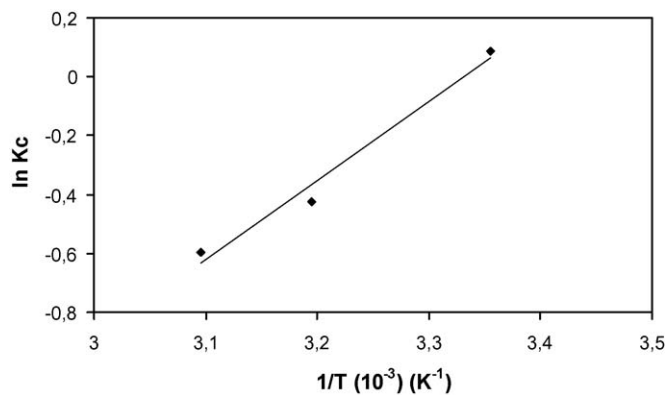
Fig. 8. Plot of ln K_C vs. $1/T$.

standard free energy ΔG^0 has negative value (-0.22 kJ/mol) at 25 °C but positive values (1.09 and 1.60 kJ/mol) at 40 and 55 °C, respectively. These results indicate that ammonium exchange by clinoptilolite is spontaneous at 25 °C. At high temperatures ammonium uptake is unspontaneous and less favorable because increasing of ΔG^0 from -0.22 to 1.09 and 1.60 at 40 and 55 °C creates an energy barrier [26,30]. In addition, at 25 °C, ammonium exchange has physical characteristic since the free energy change is between 0 and -20 kJ/mol [31].

Change in the standard enthalpy ΔH^0 indicates a negative value as -22.34 kJ/mol, therefore, ammonium exchange is an exothermic process. The negative value of the standard enthalpy change ΔS^0 (-74.42 kJ/mol) suggests that the randomness decreases the removal of NH_4^+ on the clinoptilolite [30].

4. Conclusions

Ammonium exchange by the natural Turkish clinoptilolite was studied in batch mode and found to be strongly dependent on initial concentration and contact time, and low temperature favors the ammonium uptake on the clinoptilolite. Langmuir model yield a much better ($R^2 = 0.927$–0.969) fit than that of the Freundlich model ($R^2 = 0.878$–0.952). R_L value from Langmuir isotherm and n from Freundlich isotherm indicates that the removal of NH_4^+ ions on the clinoptilolite is favorable.

The pseudo second-order kinetic model agrees very well with the dynamical data for the exchange of NH_4^+ ions on the clinoptilolite. The negative value of ΔG^0 at 25 °C indicates that the ammonium uptake is spontaneous. The negative values of ΔH^0 and ΔS^0 show that the ammonium exchange is an exothermic process and the randomness decreases the uptake of ammonium on the clinoptilolite.

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